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⑥ STUDY OF THE ELECTRONIC SURFACE STATE OF III - V COMPOUNDS.

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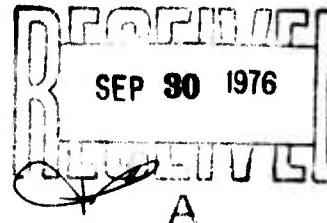
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SUMMARY

A. HIGHLIGHTS

1. For the first time it has been shown directly that Schottky barrier pinning on a III-V material is not produced by intrinsic surface states characteristic of the clean surface (as suggested by Bardeen, Mead and others) but rather is produced by states induced by the metal placed on the semiconductor to produce the Schottky barrier.

2. Since establishing this by results on GaSb, it has been shown that there are no intrinsic surface states on the (110) surface of GaAs. The Fermi level pinning which was previously observed and interpreted in terms of intrinsic states in the gap has been shown to be due to extrinsic pinning, probably due to defects.

3. It has also been shown that oxygen bonds preferentially to As and P surface atoms on GaAs and InP as was previously predicted.

4. In very recent results, it has been found that GaAs can be exposed to atmospheric pressures of O_2 without breaking covalent bonds of the GaAs or InP, e.g., the O_2 only chemisorbs on the dangling bonds associated with the surface As atoms. However, if the O_2 is excited by, for example, a hot filament or an ion pump then covalent surface bonds are broken and the surface is torn up. This has obvious applications for forming practical surfaces.

5. The surface chemistry of GaSb has been found to be very different from that of GaAs and InP. Unexcited, molecular O_2 will break covalent bonds in binding the surface atoms to the rest of the crystal and thus "tear up" the surface. In addition, Cs does not adhere as tightly to the

surface of GaSb as to that of GaAs and InP. Finally, it appears to take a much thicker layer of Cs on GaSb to reduce the electron affinity than on GaAs or InP.

B. GENERAL

Careful studies at low energy ($h\nu < 11.8$ eV) of n-type InP produced results similar to that of n-type GaAs at $h\nu < 11.8$ eV. The Fermi level is pinned on the clean surface at 0.25 eV below the CBM and application of Cs caused Schottky barrier pinning near the pinning position on the clean surface. InP is found to be extremely insensitive to oxygen and the Fermi level pinning is unaffected by this gas. Studies of n- and p-type GaSb revealed that this material is quite different from GaAs and InP. There are no pinning states in the bandgap and small amounts of oxygen or alkali metals caused the Fermi level on the n-type sample to move through most of the bandgap. When Cs was applied to produce maximum "white" light photoelectric yield from the GaSb sample, the Cs overlayer was thick and unstable. Interaction between GaSb and Cs appears weaker than that between GaAs and Cs or InP and Cs. Exposure of Cs-covered GaSb to oxygen led to photoelectron energy distribution curves (EDCs) similar to those of bulk Cs-oxide, while it took numerous cycles of oxygen and Cs treatment on GaAs to yield EDCs which are characteristic of bulk Cs-oxide.

Extensive work on the III-V compounds, GaAs in particular, has been done at the Stanford Synchrotron Radiation Project, where intense light up to several hundred electron volts in energy is available. An investigation of the chemical shifts in the core levels upon oxidation shows that for GaAs and InP, oxygen removed electrons preferentially from the surface column V elements (As and P), leaving the column III elements (Ga and In) unaffected and producing no measurable "tearing up" of the surface while for GaSb, by $5 \times 10^5 L$ O_2 ($1L = 10^{-6}$ Torr seconds gas exposure) both surface

elements are involved in the oxidation and the surface is being "ripped" apart. After studying numerous cleaves on different GaAs samples, we found that the Fermi level was pinned, right after cleaving as had been found previously, on some cleaves of some samples but not on others. One crystal showed no pinning in all four cleaves made. The unpinned samples had sharp EDCs while the pinned samples had smeared EDCs which sharpened as small amounts ($\geq$ 10L) of oxygen was added. Partial yield spectra showed little change up to 10^5L O_2 so it is concluded that the pinning on the cleaved surface was due to <u>extrinsic</u> states and that the empty surface states were located in the conduction band.

Theoretical work on the clean Si surface suggests that modification of the surface reconstruction may automatically bring the Fermi energy at the surface to midgap region even if intrinsic or extrinsic surface states are not present, i.e., in the minimum energy state of the surface, re-arrangement of atoms will take place in order to produce the pinning. The corresponding effect is not expected on polar semiconductor surfaces.

For the past several years we have been studying very carefully the cleavage faces of three III-V semiconductors; GaAs, InP and GaSb, in order to understand the electronic properties of their surfaces. Experiments were carried out on both clean and gas or metal covered surfaces, so that correlations may be made between states on the clean surface and extrinsic pinning states (e.g., Schottky barrier pinning states). These experiments were also done with determination of the best procedure for preparing practical surfaces for III-V devices in mind.

At the time of the last semi-annual report a fairly complete picture of the properties of the III-V surface had been formed. The most important result is the proposal of the GSCH model for the III-V semiconductor surface, linking the empty surface states to the surface column III atoms and the filled surface states to the surface column V atoms. A correlation was also found between the bottom of the empty surface states and the Schottky barrier pinning position in cases where the Fermi level was pinned after cleaving. At that time we believed that the Fermi level pinning on clean GaAs and InP was caused by empty surface states extending to midgap on GaAs and 0.25 eV below the conduction band minimum (CBM) on InP, while on GaSb the empty surface states lie above the CBM and the bandgap is free of pinning states. However, recent experiments by Huijser and van Laar[1] and our own work at the Stanford Synchrotron Radiation Project (SSRP) has demonstrated that E_F may be unpinned on clean, cleaved GaAs and that pinning is due to extrinsic states probably produced by surface defects. Photoemission partial yield experiments performed were important in reaching this conclusion. However, the earlier conclusions are still substantially correct although some need modification as indicated below. As the empty

1.

surface states on GaAs are now found to lie in the conduction band, this is in agreement with the GSCH model, which predicts a bandgap between the filled and empty surface states and associates the filled surface states with the column V element and the empty surface state with the column III element.

However, modification of our past interpretations is necessary in the case of the correlation between Fermi level pinning on n-type samples and Schottky barrier pinning, as extrinsic and not intrinsic surface states are now shown to be causing pinning on GaAs.

There is considerable evidence that defect states produce the extrinsic states and it is clear that surface rearrangement and strains produced by surface defects may be very important in cases where oxidation can be ruled out as causing the pinning. Oxidation studies on cleaved GaSb have suggested a possible reason for the variation in E_F pinning observed by different groups, because E_F is very sensitive to small (<< 1 monolayer) of oxygen, and presumably to some other gases as well. Recently, a very strong dependence of oxidation rate on the presence of a hot filament was found at SSRP. Since the gauge used in the GaSb studies at Stanford was a cold cathode (Redhead) gauge, discrepancies might be expected between this work and others where hot filament gauges were used and where vacuum was less well controlled.

The following chapters which consist mostly of papers published or submitted for publication, document the development of our line of research and thought on the surface electronic properties of the III-V semiconductors. Chapter II contains part of the most recent work at SSRP on all three semiconductors, showing in particular, that the pinning on clean GaAs is due to extrinsic and not intrinsic states. Chemical shift studies of the core levels are also included. The rest of the huge amount of SSRP work just

2.

completed but not yet analyzed completely will be included in the next report. Chapter III describes a definitive experiment using synchrotron radiation at about 100 eV on the oxidation of GaAs, showing from the observed core level chemical shifts with oxidation that the prediction of the GSCH model is correct, i.e., oxygen bonds on to the surface As atoms. Chapter IV deals with InP, a material which is very sililar in behavior to GaAs, and we draw much the same conclusions from a detailed study of it at low photon energies as from studies on GaAs. A partial report on this material has already been presented in the last semi-annual report; this chapter is a more complete discussion of the work. The next chapter discusses GaSb, which has quite different surface properties than GaAs and InP. Experiments done on it bring to one a sudden realization of the enormous complexity of the III-V surfaces, as much of its behavior is totally unexpected based on our experience with GaAs and InP. Thus, one must be extremely careful in making generalizations from one material to another. A theoretical study of the Fermi level pinning on semiconductor surfaces is the subject of Chapter VI, where W. Harrison shows that pinning is possible on Si and Ge without the presence of surface states in the bandgap. Our plans for the future are given in the last chapter.

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1. A. Huijser, and J. van Laar, Surf Sci. __52__, 202 (1975).

SYNCH͙   N RADIATION STUDIES OF ELECTRONIC STRUCTURE

AND SURFACE CHEMISTRY OF GaAs, GaSb, and InP

I. INTRODUCTION

The GSCH (Gregory, Spicer, Ciraci and Harrison) model for the surfaces of 3-5 compound was discussed at the 3-5 Interface Conference last year.[1] The essence of this model[2,3] was that filled and empty surface states were located primarily on the As and Ga surface atoms respectively. Further an appreciable band gap (1 eV or more) separated the filled and empty surface states. As stated last year[1] there was very strong experimental and theoretical evidence for this model. The work of the intervening year has produced added confidence in the general model.[4]

One prediction[2] on the basis of that model was that the chemical adsorption of oxygen would directly involve the surface column 5 atom (e.g., As) but not column 3 (e.g., Ga) atoms. To be more precise, if the oxygen is adsorbed without breaking covalent bonds of the GaAs, it should remove electrons from the surface As but not Ga atoms. In the intervening year we have tested these suggestions by examining the shifts in ionizing energy of the core 3 or 4d or 2p core level for GaAs,[5] GaSb and InP. A summary of the most recent of this work will be presented here.

There was also general agreement at the 3-5 Interface meeting last year,[1,6] that the Fermi level on the (110) surface of GaAs was pinned near midgap. It was assumed further that this pinning was due to the bottom of the empty intrinsic surface states. Partial yield measurements[6,7] were interpreted as giving further evidence for this. Further, correlations of various strength were made between the pinning position on clean surfaces and the Fermi level pinning position on Schottky barriers.[1,6] Several developments have cast questions on the previous results and correlations. First, van Laar and R. Huijser[8] have shown that GaAs (110) surfaces can be formed by cleaving without any pinning. Further, Chye

et al[9] have studied clean GaSb n and p type samples on which no pinning occurs and found that pinning can be produced by forming a Schottky barrier or by small amounts of oxygen. Eastman and coworkers have also reported now finding n-type 3-5's without surface state pinning.[10]

This has led us into an intensive study of the question of pinning on n-type GaAs cleaved (110) surfaces, the results of which will be reported here.

II. CORE SHIFTS ON OXYGEN EXPOSURE

If, as the GSCH model suggests, the broken bond electrons of a 3-5 surface are associated with the As surface atoms, chemisorbed oxygen on a (110) surface should gain electrons from these atoms and not from the Ga surface atoms. This, of course, presupposes that the adsorption is to take place without breaking any of the covalent bonds binding the surface atoms to the rest of the crystal.

This can be checked by examining the shift in energy of core electrons as the oxygen is adsorbed. Atoms which give up electrons to the oxygen will exhibit an increase in bonding energy of the d-core electrons. The Stanford Synchrotron Radiation Project (SSRP) provides a very convenient photon source for such studies since the "4° line" presently provides photons in the 30-360 eV range.

In Figs 1-3, we present results from GaAs, InP and GaSb. As can be seen for GaAs and InP (Fig. 1 and 2) very well defined shifts are seen for the As and P core levels without any shifts in the Ga 3d or In 4d levels.

The area under the shifted peak (as well as the area of the oxygen 2p peak at about 4 eV) indicates the amount of oxygen which has been chemisorbed. Note that under the conditions (room temperature and up to .5 Torr

5.

# OXIDATION OF n-TYPE GaAs(110) at $\hbar\omega = 100\,eV$
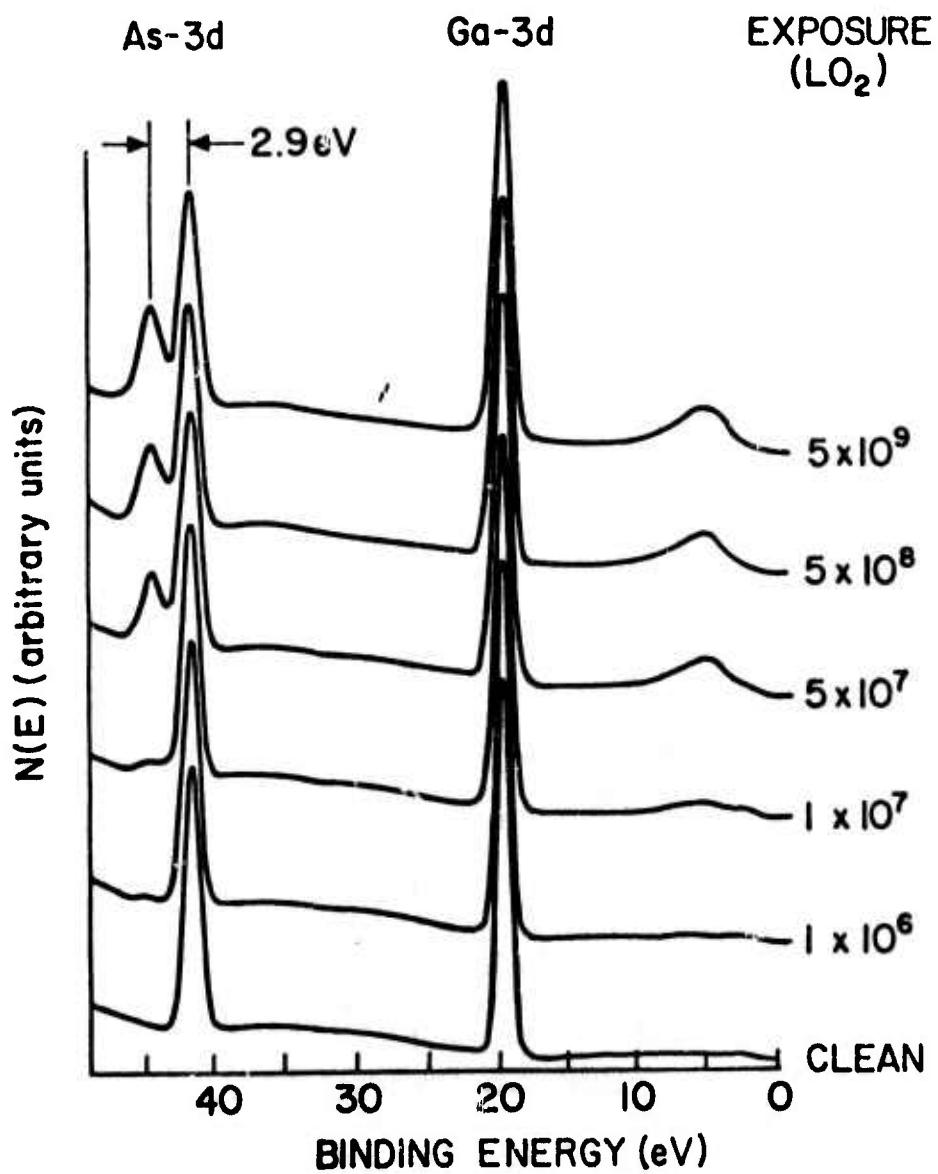
Effect of O_2 exposure on cleaved GaAs (110) at 100 eV photon energy.

FIG. 1

6.
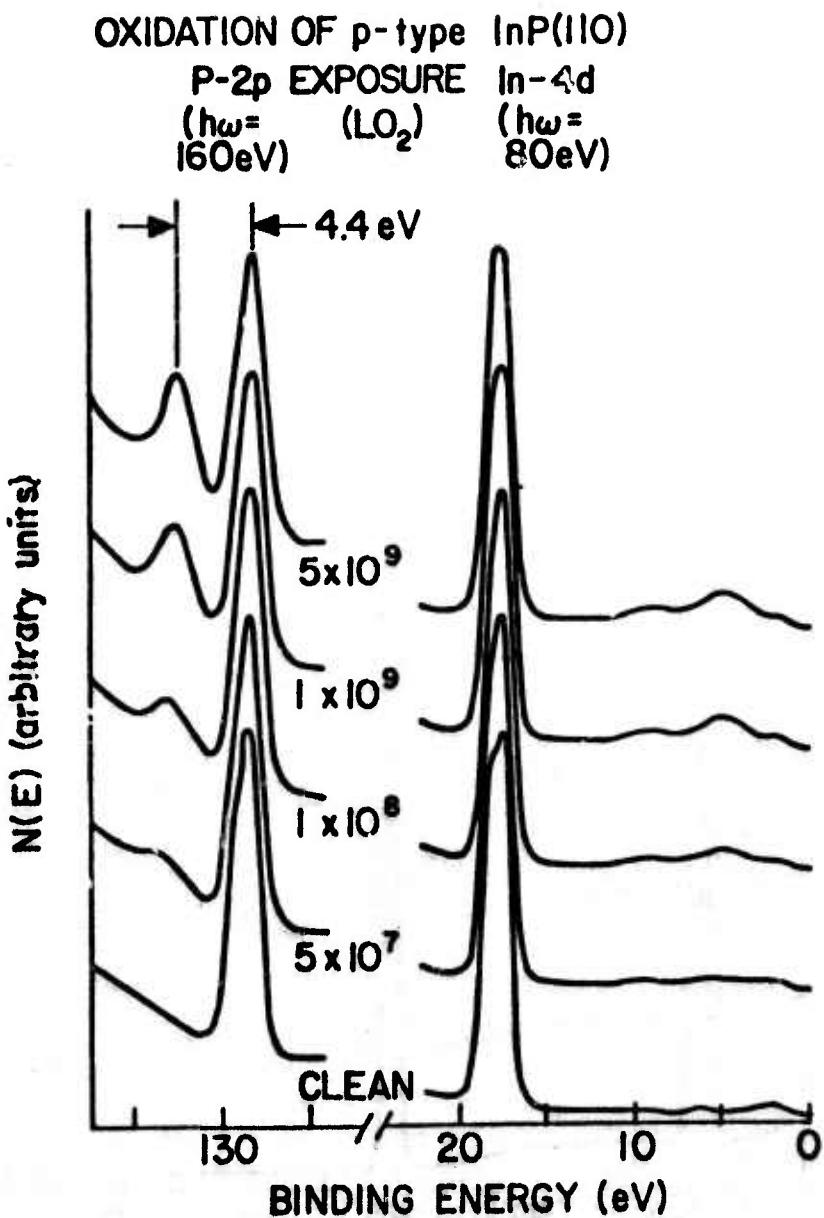
Effect of O_2 exposure on cleaved p-type InP (110).

FIG. 2

7.

OXIDATION OF n-TYPE GaSb(110) at $\hbar\omega = 100$ eV
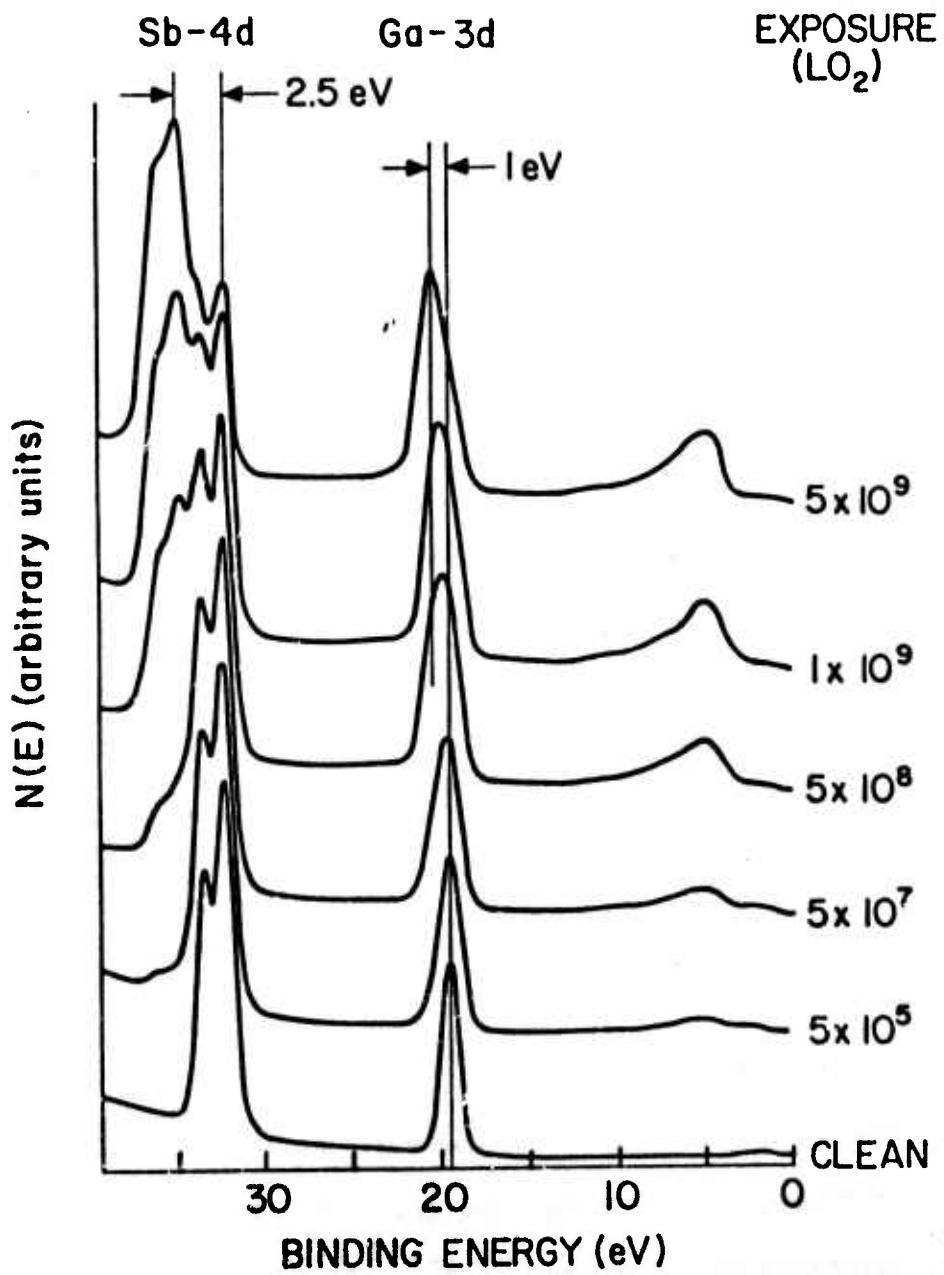
Oxidation of cleaved n-type GaSb (110) at 100 eV photon energy.

FIG. 3

8.

of oxygen) used in this experiment, the oxygen absorption saturates at exposures near 10^8L for GaAs and 10^9L for InP.

In earlier[5] GaAs experiments, a second peak with a larger shift appeared at high oxygen exposures. This peak was accompanied by a shift in the Ga 3d peak. We have now established that this was due to oxygen broken up by a hot filament ionization gauge. Based on recent controlled experiments, it seems plausible that the shifted peak was due to this oxygen attacking the bonds binding the surface atoms to the rest of the crystal.[12] When the surface is exposed to only molecular oxygen this effect is removed, and the results shown in Fig. 2 are obtained with only a single shifted As peak and no Ga shift.

The situation with GaSb is quite different from that of GaAs and InP. There is no sign of saturation and the shifted peaks continue to grow at least up to an exposure of 2 X 10^{10}L (the largest used in these experiments). Further, a Ga shift of approximately an eV is seen to accompany the Sb shift even when a relatively small Sb shifted peak has been produced (at an exposure of 5 X 10^8 Torr). From this we conclude that in GaSb, even with only the presence of molecular oxygen, the oxygen breaks bonds of Ga and Sb surface atoms with the rest of the crystal from the start of the oxygen exposure.[11,12]

III. EFFECT OF O_2 AND Cs ON FERMI LEVEL PINNING OF GaSb

It was found by Chye et al. that there was no measurable Fermi leven pinning on the clean, i.e., freshly cleaved, (110) n or p type GaSb. A preliminary report appears elsewhere[9] and a complete report is in preparation.[13] Our purpose here will be to show how the surface Fermi level pinning varies as O_2 and Cs are added to the surface. As can be seen from Fig. 4b, as the oxygen exposure is increased from 10 to 10^4L, the Fermi

9.

level drops almost the full band gap and becomes pinned near the valence band maximum. Note that the oxygen exposures which produce the Fermi level pinning are much smaller than those required to produce the core level shifts or the oxygen 2p emission (see Fig. 3). Sb d-shift and oxygen 2p build up are first detected for 5×10^5L, a factor of 50 higher exposure than that producing the .5 eV drop in E_f (Fig. 4b). Thus, the Fermi level pinning change is produced by very small oxygen coverage. Finally, note that the Cs also pulls the Fermi level down to near the valence band maximum, i.e., to almost the same position as in the case of oxygen (Fig. 4a). The final Cs pinning position correlates well with Schottky barrier studies.

IV. ELECTRONIC STRUCTURE OF THE (110) GaAs SURFACE

There is now general agreement[2,3,14] that there are no detectable filled surface states in the bandgap of the GaAs (110) clean surface in spite of earlier reports to the contrary.[15] Further, the detailed work of Gregory and Spicer[16] in the range $h\nu < 12$ eV shows that there is no appreciable filled surface state density degenerate with the uppermost 0.5 eV of the valence band. This is clearly in opposition to published band calculation results[17,18] which show very large filled density of states peaks within 0.5 eV of valence band maximum (VBM). It seems to us most likely that this difference is due to lack of knowledge of the detailed re-arrangement of the surface atoms within the unit cell. The calculations assumed no rearrangement; however, it seems much more probable that surface relaxation does take place. This would be expected to lower the filled states.

Gregory and Spicer could see no distinct structure which could be associated with a surface resonance lying deeper in the valence band in clean (110) GaAs.[16] Furthermore, they could see no distinct changes with
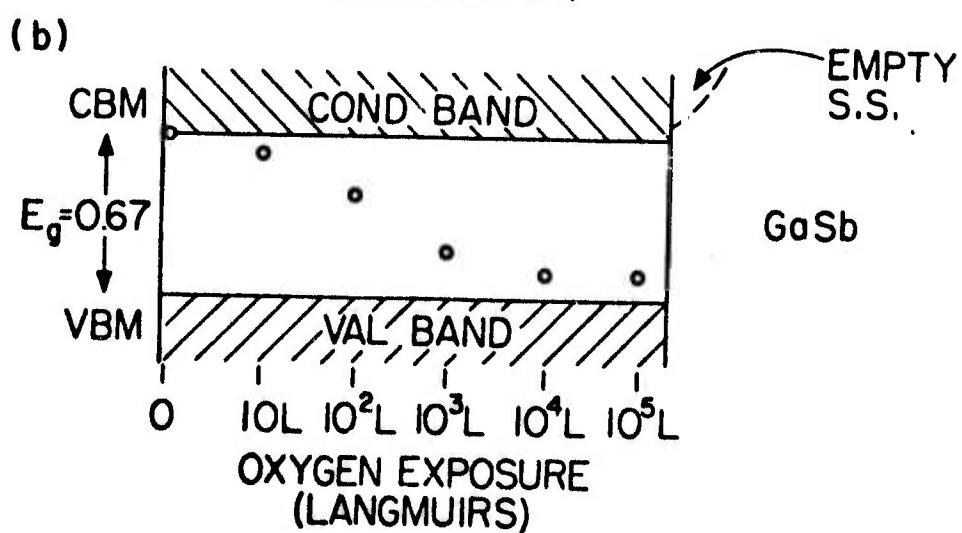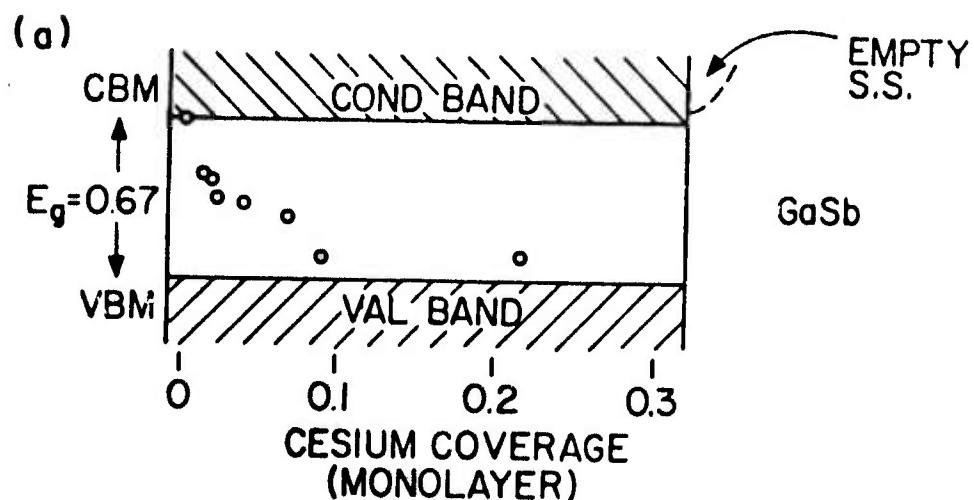
(a) GaSb (110) Fermi level pinning vs Cs coverage.

(b) GaSb (110) Fermi level pinning vs oxygen exposure.

FIG. 4

11.

gests that the surface resonances are broad and do not yield sharp structure which can easily be seen against the background of bulk valence band emission. However, oxygen produces strong and surprising effects in EDCs measured at $h\nu$ = 21eV, as will be discussed below.

Until recently, the overwhelming mass of evidence suggested that the intrinsic Fermi level pinning position was near midgap for a freshly cleaved (i.e., clean) (110) GaAs n-type sample.[20,21] The one exception was the work of van Laar and Scheer[22] which reported no pinning. The careful work of van Laar and Huijser[8] has recently confirmed the earlier work and has established that Fermi level pinning does not necessarily occur on the (110) cleavage face of GaAs. Through correspondence with van Laar and Huijser[8] and a visit to their laboratory, we recognized the possibility that the difference between their results and those in our laboratory might be inherent in the crystals themselves and not just due to differences in cleavage technique or other effects of handling and preparation. Thus, we have recently made use of a second source of crystals (Laser Diod Corp.). All of the earlier work of Gregory et al. was done on crystals obtained from MCP Electronics, Ltd (MCP) in England. Furthermore, the work we will report next was done using a new, specially designed chamber[12] and the 8° line ($6 \leq h\nu \leq 30$ eV) at SSRP. This chamber had a cleavage apparatus based on the same principle as that used earlier by Gregory et al., but with strong differences in detail. Because of the small, well focused photon beam from SSRP, the cross section of the crystal could be reduced from 1 X 1 cm to 0.5 X 0.5 cm. The new chamber designed for SSRP allowed four crystals to be cleaved and studied in the system without breaking vacuum. The base pressure of the chamber is 2 X 10^{-11} Torr; the operating pressure with all ports to the

12.

storage ring open and photons on the sample is 5×10^{-11} Torr. The same chamber was used for the studies reported in Section II of this report.

In Fig. 5 we present data obtained from ten different cleaves made on three different n-type crystals (two from Laser Diode Corp. and one from MCP). The MCP crystal was Si doped (bulk doping 1.7×10^{18} cm^{-3}) and the Laser Diode crystals were Te doped (bulk doping 3×10^{17} cm^{-3}). As can be seen, all of the cleaves from Laser Diode Crystal I (LDI) had no Fermi level pinning, i.e., the surface Fermi level was at the bulk position. In contrast, the MCP crystal had one cleave with the Fermi level at the bulk position and one with the Fermi level pinned 0.6 eV below the bulk position as was found for all cleaves from this crystal in the apparatus used by Gregory et al. From this it appears that while the method of cleaving may play a role, other, as of now, unidentified characteristics of the crystal also play a role in determining where the Fermi level, E_f, is pinned on cleaving.

In Fig. 5, we also indicate how the surface position of E_f varied with oxygen exposure. Note that for all of the surfaces which showed no pinning on cleavage, the surface Fermi level drops rather rapidly with oxygen exposure. Note in particular that the large changes in Fermi level pinning are completed by exposures of about 10^5L; whereas, from Fig. 1, it is clear that it is well above this exposure that the effects of oxygen are first seen, i.e., the Fermi level pinning is completed at coverages which are probably much less than 1% of a monolayer.

Note also the bizarre behavior of cleave B of the MCP crystal. Here E_f is originally pinned 0.6 eV below the conduction band minimum (CBM) but the pinning position rises to the bulk position for exposures between 10 and 10^2L and then drops back to close to the original pinning position

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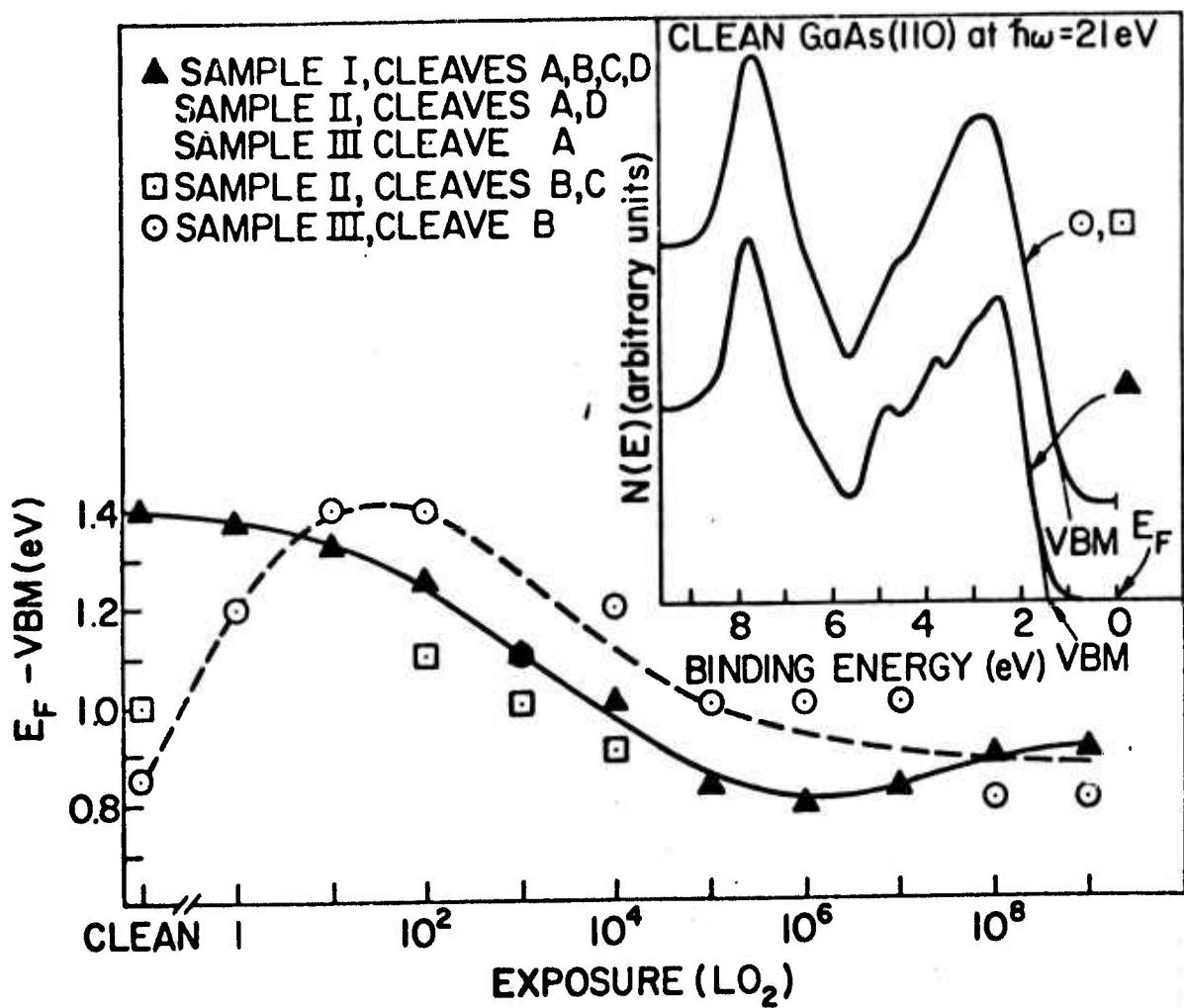
Fermi level pinning on GaAs (110) for various samples and cleaves as a function of oxygen exposure.

FIG. 5

14.

for higher exposures. No such behavior was observed in the work of Gregory and Spicer[1,19] using other cleaving apparatus and the same crystal before it was reduced from 1 X 1 to 0.5 X 0.5 cm in cross section. Rather, Gregory and Spicer found that there was little variation of Fermi level on n-type GaAs cleaved in the apparatus used by them. Note also that another cleave at SSRP on the MCP 0.5 X 0.5 crystal did not produce pinning.

In the GaSb work mentioned in Section III, it was noted that, whereas there was no surface pinning on a clean cleave, the final pinning produced by oxygen was very close to that produced by metals. The same thing is true on those GaAs which show no pinning on cleaving. The pinning position due to Cs and Au is in the range of pinnings provided by oxygen.[1,19] Note also that the final pinning position with oxygen does not depend strongly on the initial Fermi level pinning position.

Another important feature is shown in the insert of Fig. 5. This shows the $h\nu$ = 21 eV EDC from GaAs surface just after cleaving. For the cleaves where the pinning is near midgap (0.7 and 0.4 below CBM respectively for LDII, cleaves B and C and MCP, cleave B), the structure in the EDCs is quite smeared out (see note, Fig. 5) as compared to that for the surfaces which gave no initial pinning. This suggests that the pinning below the bulk position may be associated with strain in the crystal which smears out the structure in the EDCs.

Figure 6 gives even more striking information related to this pheno- mena. In this figure, we present EDCs (taken at $h\nu$ = 21 eV where the es- cape depth is probably only a few lattice spacings or less) for a crystal which showed E_f pinning at midgap (MCP, cleave B) on cleavage and one which did not show any pinning (LDII, cleave A). As can be seen, exposure

OXIDATION OF GaAs(110) at $\hbar\omega = 21$ eV

SAMPLE III, CLEAVE B

SAMPLE II, CLEAVE A

$N(E)$ (arbitrary units)

10^6 LO$_2$

10 LO$_2$

CLEAN

10^6 LO$_2$

10 LO$_2$

CLEAN

8   6   4   2   VBM   6   4   2   VBM

ENERGY BELOW VALENCE BAND MAXIMUM (eV)
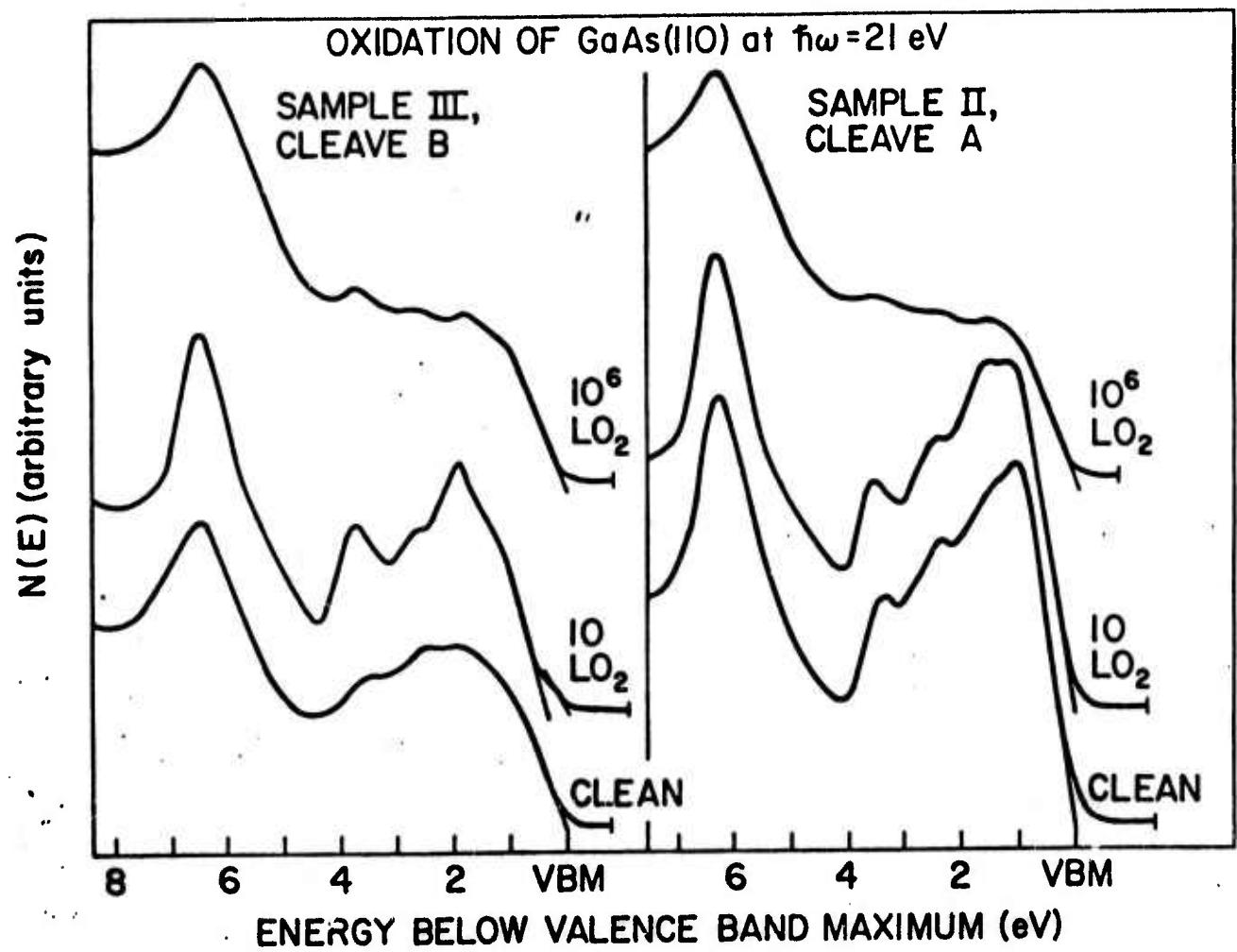
Valence band spectra showing the effects of oxygen.

FIG. 6

16.

ticular that the EDC for MCP cleave B sharpened strikingly with the small oxygen exposure and that, particularly in the range of approximately 2.5 to 1 eV below the VBM, the EDC is quite different from that of LDII, cleave A, although LDII, cleave A does also change on 10L of oxygen exposure in the energy range 1 to 2 eV below VBM. Note also that these changes take place at exposures many orders of magnitude below those necessary to cause a measurable shift in the As 3d levels or a measurable oxygen 2p emission (see Fig.1). Thus one must conclude that these large changes in the EDCs are caused by secondary effects of the oxidation such as a change in rearrangement of the atoms within the unit cell perhaps due to the removal of dislocation pinning. Further, the data si $\simeq$ a strong sensitivity in the energy range 1 to 2.5 eV below VBM, suggesting that surface resonances may be particularly strong in that region.

Finally, note that for exposures of 10^6L (where the changes in Fig. 1 are first becoming apparent) the structure in the EDCs is strongly washed out and the two EDCs look quite similar. It is at this exposure where the E_f pinning is similar for the two samples and the shift in As 3d and oxygen 2p levels are just becoming detectable (see Fig. 1).

V. PARTIAL YIELD STUDIES

It now appears that the partial yield measurements introduced by Eastman and Freeouf[7] in their studies of 3-5's are affected in an important way by excitonic interactions[9,23] and thus can not be explained solely in terms of one electron density of states as originally proposed.[6,7,14] However, this technique presently provides the only means using photoemission for directly measuring optical transitions involving the intrinsic empty surface states. Even though the excitonic effects prevent

17.

intrinsic states, they should allow us to detect any massive movement in energy of these states. For example, in Fig. 5, the surface Fermi level position varies by a half eV or more for the various samples, cleaves, and oxygen treatments. Is this movement due to a massive movement of the intrinsic surface states caused by, for example, relaxation of the surface atoms or is it due to changes in pinning by extrinsic states? Partial yield measurements give us an opportunity to answer this question. If there is a movement of the intrinsic surface states by tenths of electron volts, one would expect this to be reflected in a movement of structure in the partial yield spectra. Since the excitons are "tied" to the bottom of the empty intrinsic surface states, any movement of this minimum would be expected to produce a movement in the partial yield structure. Correspondingly, if the empty intrinsic surface states were located at different positions on different crystals corresponding to the different surface E_f positions (see Fig. 5), the partial yield structure should occur at different values of $h\nu$.

Partial yield results are presented in Fig. 7 for two cleaves of different crystals where the initial pinning position (see Fig. 5) varies by about 0.5 eV and where the behavior of E_f with oxygen exposure is quite different. As can be seen, the partial yield structure is strikingly independent of the pinning position on the freshly cleaved surfaces and does not change in position with oxygen exposure. This indicates that it is not differences in the intrinsic surface states which cause the differences in E_f pinning but rather, these differences must be due to extrinsic effects.

Note that the sharp structure in the partial yield is smeared out by O_2 exposures of 10^6 to 10^7 L O_2. This is just the range of exposure in which the surface adsorbs a significant fraction of a monolayer of O_2.[24] It is also

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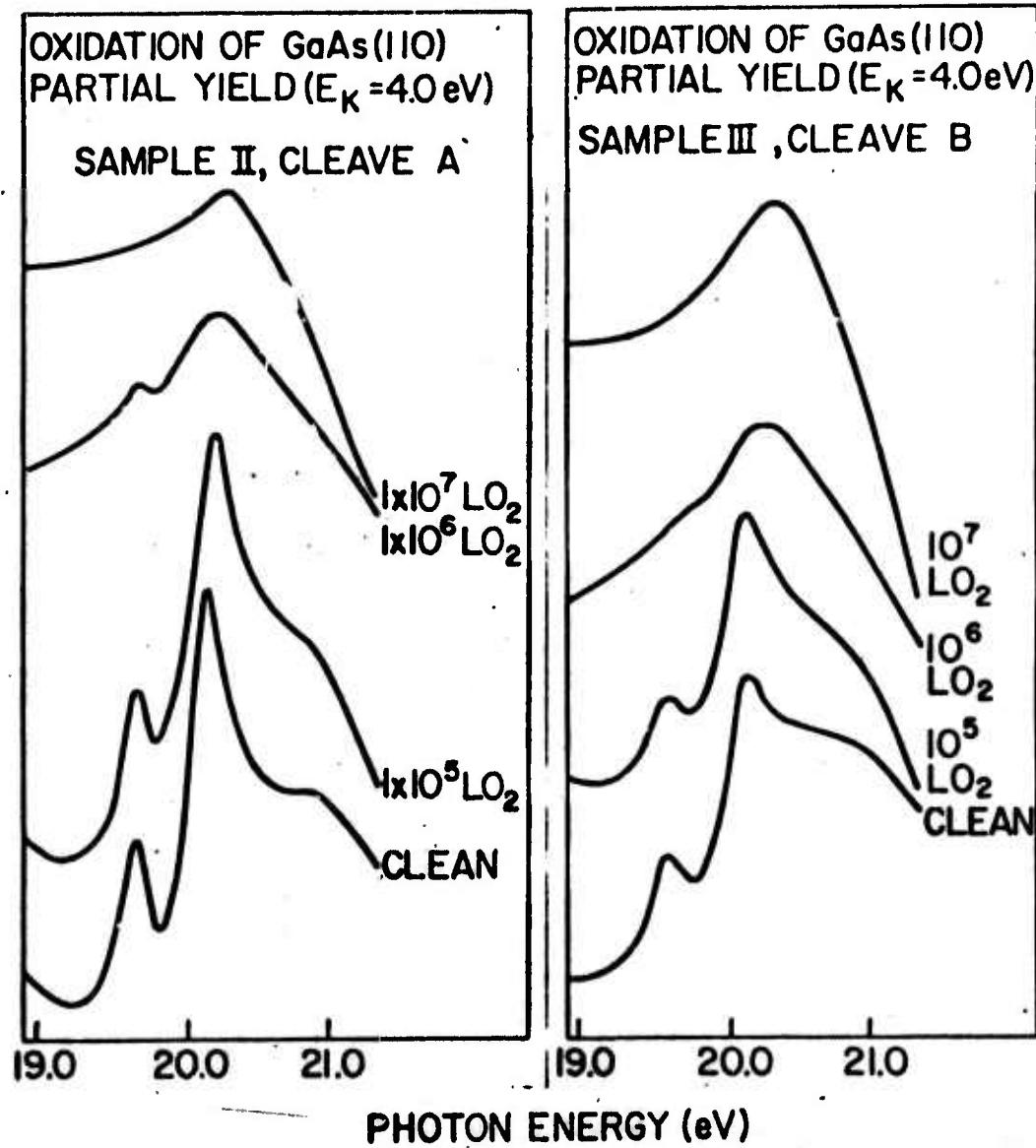
Partial yield spectra of GaAs (110) with 4 eV final state energy.

FIG. 7

19.

This suggests that the adsorbed O_2 disturbs the final state with which the exciton is associated. However, since the intergal under the partial yield curves is not greatly affected by the smearing and since the principal peak at about $h\nu = 20.2$ remains even though broadened, it appears that the transitions are smeared but not removed and that the empty states on the Ga are not destroyed. Similar results are seen on bulk excitons as the perfection of the crystal is disturbed.

VI SUMMARY, DISCUSSION AND CONCLUSIONS

A. Cause of Fermi Level Pinning on Clean (110) GaAs Cleavage Surfaces

Three different GaAs crystals from two sources (MCP and Laser Diode) have been placed in the same vacuum chamber and, without breaking vacuum, cleaved (110) and studied with photoemission ($9 \leq h\nu \leq 360$ eV) to obtain the surface Fermi level (E_f) position and to study electronic structure near the surface. These results have been correlated with prior results obtained using crystals from only one source (MCP) and a different apparatus.

Under these conditions it is found that:

1. The surface Fermi level pinning position varies from the conduction band minimum, CBM, (i.e., the bulk pinning position) to mid gap.

2. Four cleaves on one Laser Diode crystal all gave no pinning, i.e., E_f was at the CBM, whereas one out of two cleaves on a MCP crystal gave pinning at 0.6 eV below the CBM where previous work in different apparatus had always found E_f pinned. A second Laser Diode Co. crystal (II) gave pinning at the CBM and 0.4 eV below CBM on different cleaves.

3. When the pinning was near mid gap, the EDCs for $h\nu = 21$ eV (where the excape depth is small) were badly smeared out; whereas, when there was no pinning, the 21 eV EDCs gave sharp structure (see Figs. 5 and 6).

4. Very small oxygen exposures ($> 10^5$ times less than that necessary to approach a half monolayer of adsorbed oxygen) strongly sharpen the "smeared out" EDCs. The same exposure causes measurable but much less pronounced changes in "sharp" (unpinned) EDCs.

5. Relatively small O_2 exposures cause measurable changes in E_f. Exposures about 10^2 less than that necessary for half monolayer coverage produce E_f pinning near mid gap on all cleaves.

We suggest that the occurrence of "smeared" out EDCs on cleavage is an indication of rather uniform and large strain in the surface region, and, thus associate the pinning near mid gap with this strain. It appears that relatively small amounts of oxygen (or, as found by Gregory and Spicer Cs) can relieve this strain. However, Gregory and Spicer[19] did not find that this removed the surface E_f pinning as was found in the work reported here.

The fact that the occurrence of surface pinning on clean (110) surfaces varies so much from crystal to crystal suggests that it is affected by strains or other unidentified qualities of the crystal as well as by the details of the cleavage procedure.

Partial yield measurements were used to determine whether or not massive changes in the position of the empty surface state band accompanies variation in E_f pinning. The results were negative. The partial yield structure associated with excitation from the Ga 3d to the empty surface states was found to be independent of the E_f pinning position and thus the occurrence and variation in pinning could not be associated with intrinsic empty surface states.

21.

As a result of the findings described above it is concluded that where pinning is found on (110) n-type GaAs cleavage surfaces, it is extrinsic in nature and associated with a relatively small number of states produced by strain or other factors at the surface. (Our preliminary investigations suggest that such strain can exist even when the cleavage faces are relatively free of steps and our knowledge of the work of others as well as ourselves indicates that a comprehensive and general relationship between cleavage "steps", pinning, "smearing" of the EDCs, and surface E_f pinning has not yet been established; however, perhaps this may develop during the 3rd 3-5 Interface Conference.)

We call attention to the possible rearrangement of the surface atoms within the unit cell either after cleaving or upon the addition of small amounts of foreign atoms (such as oxygen or Cs) to the surface. We note that the "smeared" EDCs may be caused by strain related to non-ideal re-arrangement. The need for very high quality LEED studies to investigate this effect is recognized.

b. Location of Surface States

Very careful studies of Gregory and Spicer in the $h\nu < 12$ eV range gave no clear evidence of filled surface states and gave particular evidence against their occurrence within 0.5 eV of the VBM. From this data we conclude that the filled surface states (associated with the As surface atoms) lie well below the bandgap and are degenerate with the bulk states forming rather broad resonance states which are hard to distinguish from the bulk states. In the present studies, higher values of $h\nu$ were used, reducing the escape depth and it has been found that in the region 1 to 2.5 eV below the VBM, the EDCs are particularly sensitive to very low (10L) exposures of oxygen. We estimate the oxygen adsorption due to

22.

10L exposure to be too small to directly affect the surface states. Thus, we associate the changes primarily with the effects of rearrangement within the unit cell. The fact that the small oxygen exposures perturbs most strongly states 1 to 2.5 eV below the VBM suggests that the surface resonances may be especially strong in this region and especially sensitive to surface strain, atomic rearrangement or related effects.

Further it is noted that the structure in the EDCs has almost disappeared at 10^6L exposure (Fig. 6) that very little oxygen has adsorbed at this exposure (an order of a few percent, see Fig. 1). Again these changes cannot be attributed to direct removal of states by the oxygen but must be associated with oxygen induced strain effects presumably associated with the surface atoms attempting to rearrange themselves on oxygen adsorption. The combined partial yield and Fermi level pinning data indicates strongly that empty surface states are located in the conduction band.

On Si, Fermi level pinning tends to be reduced or removed by surface oxidation.[25] This is essential to the production of useful MOS devices. Figure 8 shows that the reverse is true on the (110) surface of GaAs. In Fig. 8, we show the surface Fermi level pinning position for p[1,3,19] and n-type GaAs cleaves (where there is no pinning on the freshly cleaved surface) as a function of oxygen exposure. For both types of doping, oxidation causes pinning. In view of this, it is not surprising that there has been so much difficulty in developing practical GaAs (or other 3-5 compound) MOS devices. It is interesting to note that for both GaAs and GaSb surfaces, the Schottky barrier pinning positions tend to fall in the range of pinning produced by oxygen.

The data of Fig. 1 confirms the GSCH model of the surface and indicates that the oxygen takes electrons from the As surface atoms. In Fig. 9, we

23.
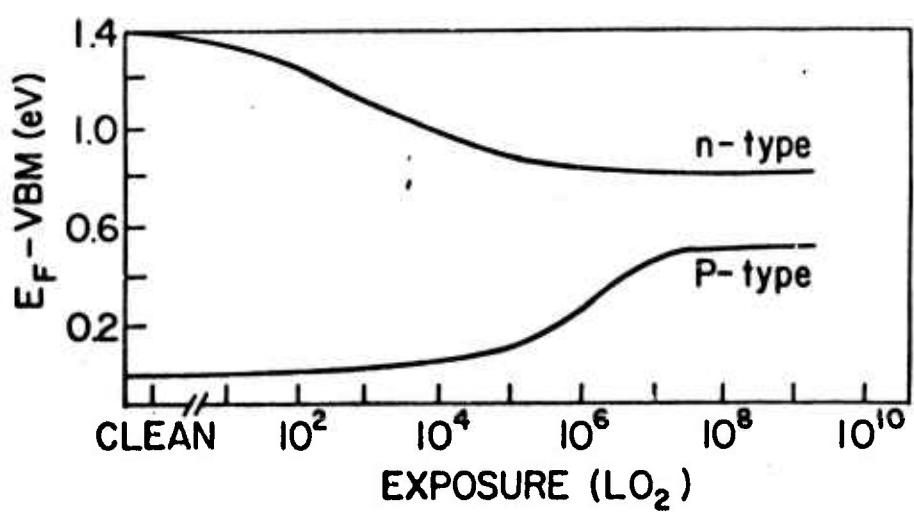
Fermi level pinning of n- and p-type GaAs (110) as a function of oxygen exposure.

FIG. 8

VB

CB

Ga As

FILLED SURFACE
STATES (As)

EMPTY SURFACE
STATES (Ga)

$2\bar{e}$ $2\bar{e}$ $2\bar{e}$

SURFACE

CRYSTAL
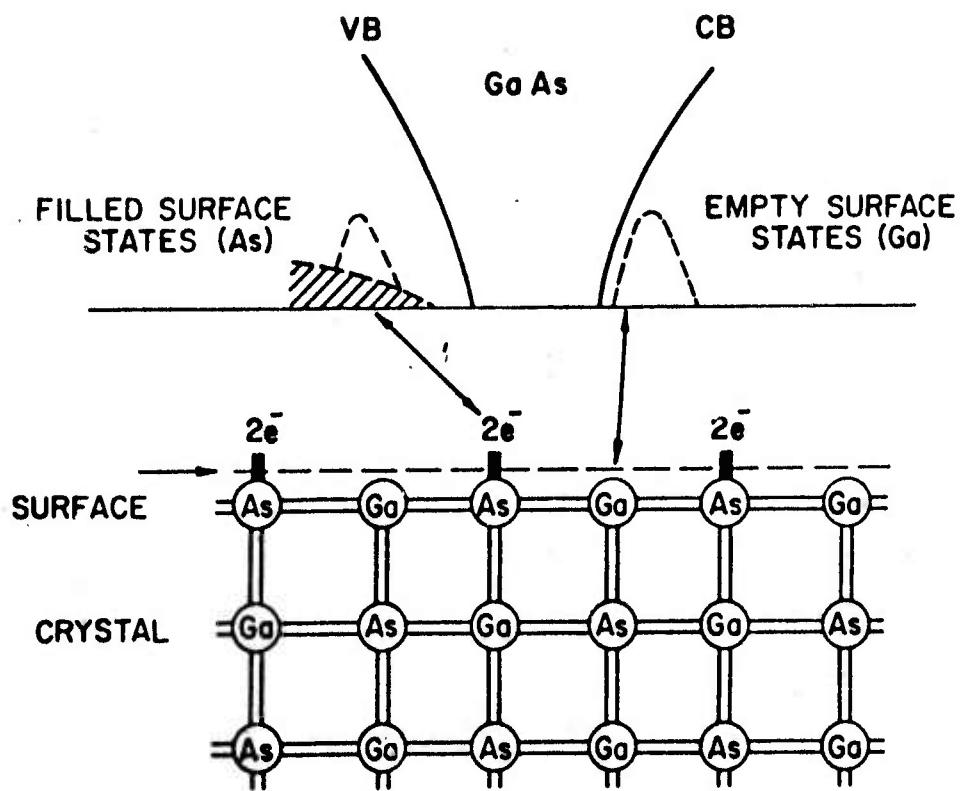
Model for the GaAs (110) surface.

FIG. 9

25.

indicate a modified model for the GaAs (110) surface. A hump in the filled density of states is placed 1-2.5 eV below VBM to indicate the especially strong sensitivity of O_2 found in that region. No quantitative importance should be applied to the size or shape of this "hump".

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CHAPTER 3

DETERMINATION OF THE OXYGEN BINDING SITE ON GaAs (110)
USING SOFT X-RAY PHOTOEMISSION SPECTROSCOPY

I. INTRODUCTION

When the work described below was done, a hot filament gauge was used which accelerated and changed the oxidation process. Later experiments (partly described in the previous chapter) show that GaAs can be exposed to 10^{12}L O_2 without breaking covalent bonds and the O_2 only chemisorbs on the dangling bonds associated with the As surface atoms. The hot filament gauge excites the O_2 so that it is now able to break the covalent bonds and "tear up" the surface, leading to Ga 3d core shifts in the curves shown in this chapter. There is no such shift without excited O_2.

II. EXPERIMENT AND DISCUSSION

In the past few years, a question has been raised concerning the binding site (or sites) of oxygen on Gallium Arsenide. The answer to this question is important not only because it will help clarify some aspects of the various GaAs surface state models, but it will also help in the understanding of the passivation of practical GaAs surfaces. In addition it provides a test of the applicability of different techniques for studying the oxidation properties of other III - V compounds as well as semiconductors in general. Furthermore, the behavior of GaAs during oxidation illustrates the way in which the surface chemistry of a covalent compound can differ from that expected from bulk heats of reaction and thermodynamic arguments. The oxidation of GaAs has been studied extensively by UPS,[1] ellipsometry,[2] electron energy loss spectroscopy (ELS),[3,4] Auger

electron spectroscopy (AES),[2,4] low energy electron diffraction (LEED),[2] and flash desorption.[5] Recent work by Dorn et. al.,[2] Froitzheim and Ibach[3] and Gregory et. al.[1] on the non-polar GaAs(110) cleaved surface suggests that oxygen binds preferentially to the surface Arsenic atoms whereas studies on polar GaAs surfaces by Ludeke and Koma[4] and Arthur[5] imply that oxygen sticks to the surface Gallium atoms. Since the reported results are from different surfaces and from surfaces prepared in different ways, caution must be exercised in generalizing the conclusions from one system to another.

It is a well known fact that inner core levels shift in energy as a function of chemical environment. This chemical shift has been used extensively in the field of x-ray photoemission spectroscopy as an aid in determining numbers of bonding states as well as the amount of charge transferred upon formation of various chemical bonds.[6] The results presented here use the chemical shift information from the 3d levels of Gallium and Arsenic to study the bonding states of the Gallium and Arsenic atoms during the oxidation of the GaAs(110) surface. Furthermore, the shorter escape depths for electrons photoemitted from the As and Ga 3d levels by photons in the range 80 to 350 eV give a significant increase in surface sensitivity over conventional XPS techniques employing $A\ell\ K_{\alpha}$ radiation.[7]

The apparatus used in these studies consists of an ultrahigh vacuum system (base pressure $<6 \times 10^{-11}$ torr) with a double pass cylindrical mirror analyzer, a multisample holder, a cleaver, Au and Cu evaporation sources and gas handling facilities. As a light source, we used synchrotron radiation at SSRP (Stanford Synchrotron Radiation Project) emitted from the storage ring SPEAR at the Stanford Linear Accelerator Center. The general properties of synchrotron radiation as well as the relevant

SPEAR parameters have been discussed elsewhere.[8] The monochromator that was used for these studies is of the grazing incidence type and is also described elsewhere.[9] We were able to obtain useful radiation for photo-emission experiments in the photon energy range from 32 to 350 eV at a resolution of 0.1 Å.

The GaAs samples were 5 x 5 x 13 mm with the long axis along the (110) direction. The p-type samples were Zn doped with $p = 6 \times 10^{18}$ cm^{-3} and the n-type samples were Te doped with $n = 3.5 \times 10^{17}$ cm^{-3}.

The measurements were done by first cleaving both the n- and p-type samples _in situ_ ($p < 1 \times 10^{-10}$ torr) and taking a set of electron distribution curves (EDC's) for different photon energies. Then, the samples were simultaneously oxidized and a set of EDC's was taken after each exposure. Spectra from freshly evaporated gold films were routinely taken to determine the Fermi level of the GaAs. The samples were oxidized using ultrapure oxygen admitted through a bakeable leak valve. The oxygen pressures during exposure ranged from 1×10^{-8} to 1×10^{-2} torr depending on the exposure. In all cases the oxygen was pumped out before the measurements were made. We cleaved each sample and performed the oxidations three times to insure reproducibility. During studies of the clean and oxidized surfaces, the base pressure while open to the monochromator and storage ring was 6×10^{-11} torr. The EDC's were taken using pulse counting and signal averaging. Each sweep was no longer than 50 seconds to minimize any intensity fluctuations from the storage ring.

In Fig. 1, we show EDC's for the oxidation of p-type GaAs taken at a photon energy of 100 eV. The spectra extend from the Fermi level (taken as zero binding energy for the clean GaAs) to a binding energy of about

31.
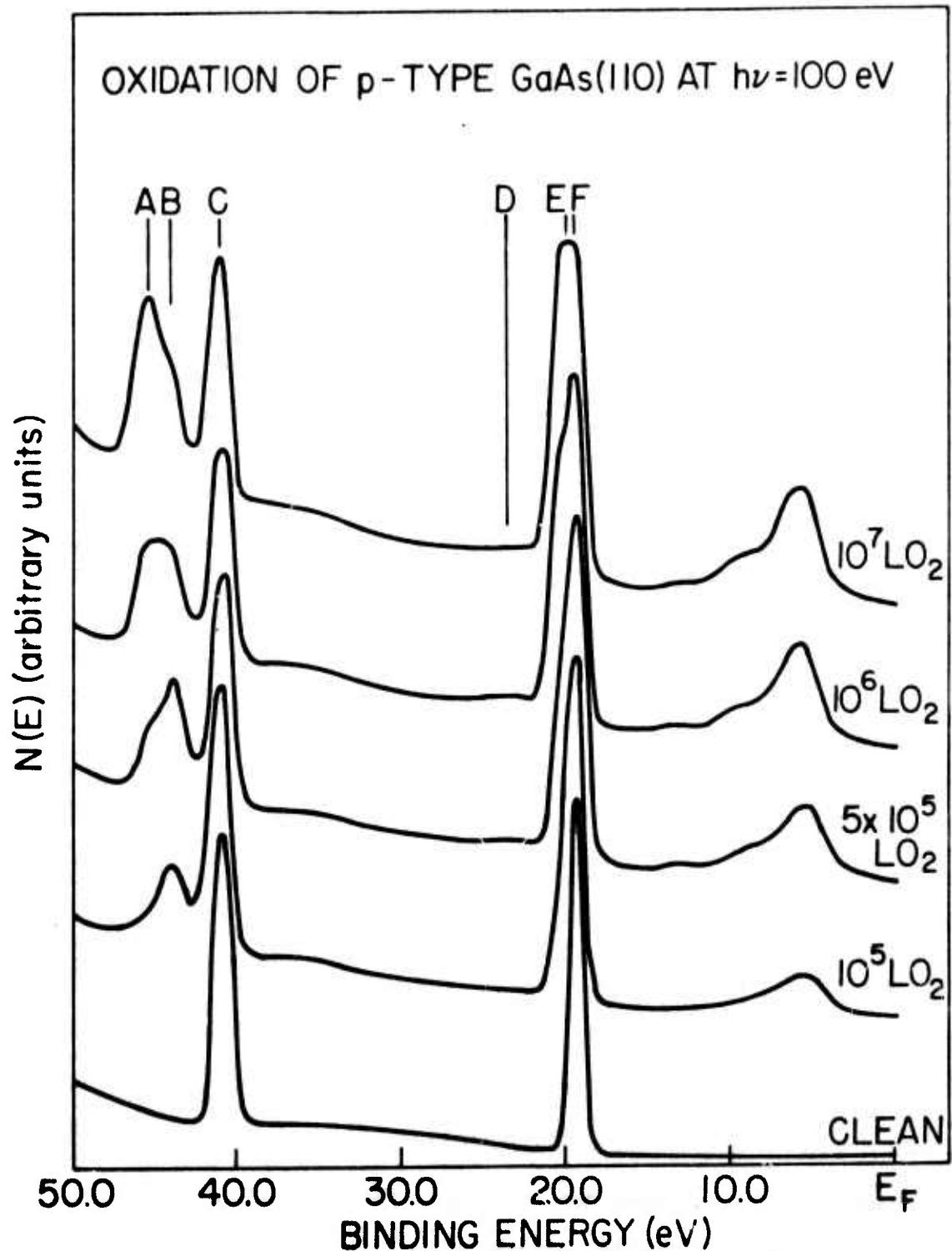
FIG. 1   Photoemission spectra of clean and oxidized GaAs (110) for
         100 eV photon energy.

50 eV. The spectra for the oxidized GaAs were all referred back to the clean spectrum. We choose to illustrate the oxidation at 100 eV photon energy because the combination of cross-section and surface sensitivity are optimum for both the Ga and As 3d levels. The bottom curve shows the spectrum for clean GaAs(110). The Ga 3d level appears at a binding energy of 19.0 eV (peak F) and the As 3d at 40.8 eV (peak C). The binding energies could be determined to an accuracy of better than ±0.2 eV. Spin orbit splitting of the Ga 3d level was not seen here because the resolution was 0.25 eV, however, it was clearly resolved at lower energies with an experimental resolution of 0.1 eV.[10] The sharpness of the Ga 3d levels in the high resolution data provides evidence that there is no measurable shift (>0.1 eV) between surface and bulk Ga 3d level (see discussion on escape depth below). Little emission from the valence band, which extends down to 13 eV below E_F is visible on the clean sample. The next curve shows the spectrum after an exposure of $10^5 LO_2$ (1L = 10^{-6} torr-sec). In this case, the two most striking features are the increase in the valence band emission, which will not be discussed here,[10] and the appearance of peak B on the high binding energy side of the As 3d level. This shift is measured to be 3 eV. Note, however, that the Gallium peak remains   less affected. Upon higher exposure, peak A appears, shifted from the As 3d level by 4 eV. Peak A first appears at 5×10^5 LO_2 and grows quickly until at 10^7 LO_2 it completely dominates peak B, which seems to stop growing as soon as peak A appears. As peak A appears, the Ga 3d level starts to broaden and at the highest exposures has split into the shifted peak E and the unshifted peak F. The best estimate for this shift is about 1 eV whereas Schön reports a shift of 1.9 eV for oxidized Ga.[12] The very small peak at 24 eV (peak D) has tentatively been

33.

identified as either O 2s or chemically shifted Ga 3d at a very low

concentration. The n-type GaAs(110) showed the same qualitative behavior

as the p-type.[11] As mentioned above, 5×10^5 LO$_2$ is the exposure at which

both peak A appears and peak E becomes discernable. This exposure also

signals the beginning of the Fermi level pinning on p-type GaAs(110),[1,10]

as well as being the point at which a significant fraction of a monolayer

starts to form on the surface of the sample.[2]

These spectra clearly show that at low coverages ($\leq 10^5$ LO$_2$), the

oxygen bonds principally to the Arsenic and leaves the Gallium less affected.

At higher coverages, the oxygen still bonds preferentially to the Arsenic,

but in a different way, as evidence by the appearance of peak A. One could

speculate on the causes of these differences (e.g., O$_2$ versus O adsorption,

interaction between adsorbed species at high coverage, etc.) and clearly

an understanding of the details in Fig. 1 should ultimately give us

detailed knowledge of the early steps in GaAs oxidation. However, the

principal focus at this time should be the fact that for all coverages

studied, the As d shift is several times larger than the Ga shift. This

provides definitive evidence that the oxygen bonds primarily to the surface

As atoms at these exposures.

The bonding of oxygen primarily to As is in accord with and predicted

by the surface state model proposed by Gregory, et. al.,[1] in which the

dangling bond electrons are localized on the As atoms and only empty

surface states are on the Ga atoms. This model has been well confirmed.[1,14,15]

Based on thermodynamical arguments and the heats of oxidation of Ga and As,[13]

one might expect that oxygen would preferentially attach itself to Ga even

at the lowest possible exposures. This does not occur because the surface

atoms are not in their elemental state due to bonding with their neighbors.

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Because of these bonds and the atomic potentials of Ga and As, it is the surface As and not Ga atoms which have "dangling bond" electrons available for the oxygen.

Now the effects of escape depth will be discussed briefly with reference to the heavily oxidized GaAs(110) of Fig. 2. This figure shows spectra from 10^7 LO_2 on n-type GaAs as a function of photon energy from 80 to 240 eV. The effect of escape depth is most clearly seen by looking at the ratio of peaks AB and C, and by remembering that peaks AB have been shifted by surface oxidation and peak C is representative of the bulk. Peaks A and B are no longer resolved because these spectra were taken at a much lower resolution. The reason for concentrating on the ratio of peak AB to C is that the effects due to cross-section changes for different photon energies are minimized. Below 90 eV the As 3d cross-section is reduced and the background of inelastically scattered electrons tends to obscure the As 3d emission. At 80 and 100 eV, peaks AB and C are approximately equal in height, indicating equal surface and bulk contributions since by 10^7 LO_2 a saturation coverage of about 0.5 monolayer has been reached. This coverage corresponds to one oxygen for each Arsenic.[2] As higher photon energies are used, the surface contribution becomes smaller as indicated by the relative decrease in peak AB with respect to peak C. At even higher photon energies on the order of 1000 eV, it is known from escape depth curves[7] that the surface contribution will appear to be negligible. This clearly illustrates the importance of being able to tune the photon energy to a range that will give minimum escape depths for the core levels being studied.

We have studied the oxidation of GaAs(110) by looking for chemical shifts in the Ga and As 3d levels. We chose a photon energy to maximize
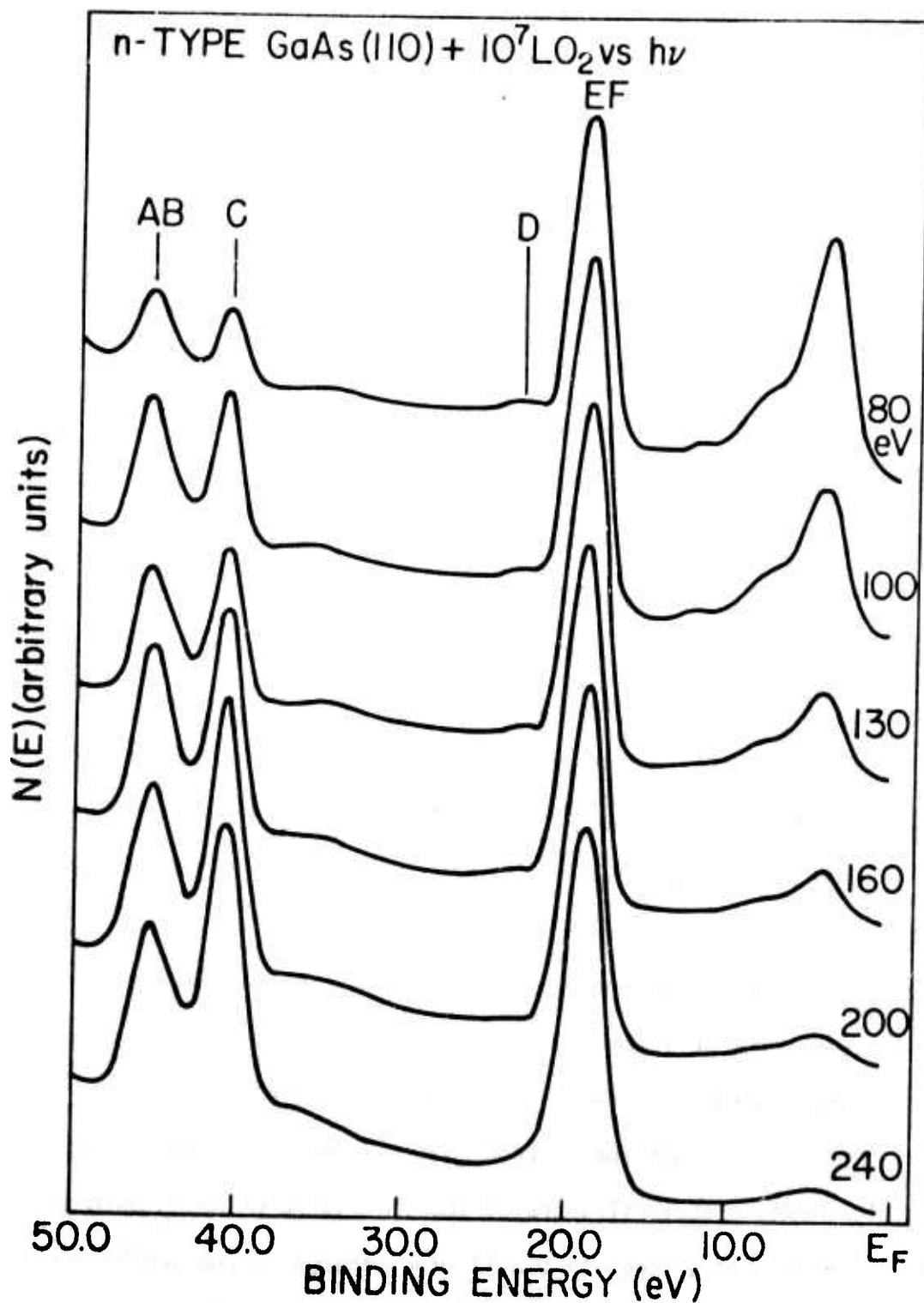
FIG. 2 Photoemission spectra of heavily oxidized GaAs (110) as a function of photon energy.

the surface sensitivity of our measurement and observed a much larger chemical shift for the As 3d level than for the Ga 3d even at relatively low O_2 coverages. The larger As shift is attributed to predominant bonding of oxygen to the As surface atoms in chemisorbing the first half monolayer of oxygen on the GaAs(110) surface. These results illustrate a very important aspect of the surfaces of covalent compounds - the chemical nature of the surface atoms, as seen by adsorbed gases, can differ drastically from that of the elemental atoms. In the present case, because of the bonding of the surface atoms to the rest of the crystal, the chemistry of Ga and As surface atoms are reversed, i.e., As has excess electrons and is oxidized first; whereas, the surface Ga has no excess electrons and behaves as a non-metallic element. The results presented here also have shown the importance of tunable synchrotron radiation in studying various gas sorption and oxidation problems by choosing a photon energy for optimum cross section and surface sensitivity. These methods should be applicable to the study of adsorption on many other systems.

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CHAPTER 4

PHOTOEMISSION STUDIES OF SURFACE STATES
AND SCHOTTKY BARRIER FORMATION ON InP[*]

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Fermi level pinning by empty surface states was observed on clean n-type InP using photoemission. Exposure to up to 10^7 Langmuirs ($1L = 10^{-6}$ Torr sec) of oxygen did not remove the pinning. The Cs-InP Schottky barrier pinning position showed good correlation with the pinning on the clear surface; however, the Cs-InP interaction was complex. The detailed movement of the Fermi level with increasing Cs coverage was complicated and could not be explained simply in terms of filling of empty surface states by Cs electrson. In addition, a large movement of the upper edge of the EDC's (Photoelectron Energy Distribution Curves), that is, the valence band edge at the Cs-InP interface, into the bulk bandgap was observed. Thus, while empty surface states may be important in determining the Fermi level pinning in Schottky barriers, other interactions will also have to be considered.

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I. INTRODUCTION

Ultraviolet photoemission spectroscopy (UPS) has proven to be a powerful tool in the study of surface electronic states. Filled surface states have been observed directly using UPS,[1,2] and information on empty surface states may also be obtained by studying the pinning of the Fermi level at the surface by these empty states.[3] Continuous monitoring of the formation of Schottky barriers is also possible with UPS by following the changes in the photoelectron energy distribution curves (EDC's) and the Fermi level pinning positions while small quantities of a metal (Cs) are being added to the surface.[4] This approach yields information during the formation of a Schottky barrier, whereas conventional Schottky barrier experiments[5]--which are performed with the metal-semiconductor contact completed--do not and thus fail to link states on the clean semiconductor surface and the metal covered surface.

While UPS is able to locate the Fermi level to a high degree of accuracy and a considerable amount of information may be extracted from changes in the Fermi level pinning, it is unable to shed light on the energy density of the pinning states except right at the lower edge.[6] Eastman and Freeouf[7] have developed a new spectroscopic technique for probing empty surface states, which they called photoemission partial-yield spectroscopy (PPYS). While they are able to determine the density of states of the empty surface state levels, excitonic effects[8] may change the measured empty surface state position.

There have been a number of theoretical[3,9-11] and experimental[1-4,7,12-14] work on intrinsic and extrinsic surface states. On the clean surface, there is now general agreement that on Si (111) 2 × 1 surfaces there is

40.

a band of filled surface states extending about 0.3 eV into the bandgap, with a peak 0.5 eV below the Fermi level. On the (110) face of III-V semiconductors such as GaAs, there are two kinds of surface states, filled and empty, associated with the two different kinds of atoms on the surface. The empty surface states are associated with the column III atom and the filled surface state associated with the column V atom. The empty surface states lie in or near the bandgap while the filled surface states usually lie below the valence band maximum (VBM). The work reported here in InP shows agreement with this general picture.

II. EXPERIMENTAL

The experimental setup was similar to one described previously.[4] Clean surfaces were obtained by cleaving the crystal (n-type InP, carrier density 6×10^{17} cm^{-3}), exposing the (110) face. A total of five cleaves were studied. A shield was mounted on the anvil to prevent the cleavage chip from flying forward onto or into the collector can. By substituting a copper emitter for the InP, the system may be calibrated so that the Fermi level could be determined to within ± 0.1 eV on the InP EDC's.[1] Oxygen exposures were made by leaking in research purity oxygen obtained from Matheson Gas Products through a Varian leak valve and carefully monitoring the pressure with either a Redhead gauge for small exposures or a millitorr gauge at large $(p > 10^{-5}$ torr) exposures. By passing current through channels containing cesium chromate and silicon, well controlled amounts of Cs may be deposited on the semiconductor surface at room temperature. The deposition process was monitored by measuring the photoyield of the sample at photon energies near

threshold. For the final exposure, light from a high intensity W-lamp was used, and the sample was cesiated to attain maximum yield. It was not possible to ascertain directly the amount of cesium deposited, but an estimate may be made by using the changes in work function in cesiated InP and published data relating cesium coverages to changes in work function for GaAs,[15] making the not unreasonable assumption that InP is quite similar to GaAs. One must, however, recognize that an error perhaps as large as a factor of two may be introduced. The coverage to give maximum "white light" response is assumed to be the same as GaAs which is about one third of a monolayer, where a monolayer of Cs is defined to correspond to a Cs atom for each surface In or P atom. The coverages used throughout this paper are all estimated values based on the method outlined above. The work function may be obtained from yield threshold measurements after correcting for the position of the Fermi level at the surface. This correction is necessary because yield thresholds are measured from the Fermi level. Photoyield of the sample was measured from threshold to 11.6 eV for each surface condition; corrections were made for the reflectivity of InP and the transmission of the LiF window. The reflectivity data was taken from Cardona's[16] measurements; the window transmission was measured separately. A calibrated Cs_3Sb photodiode was used as a standard in the yield measurements. The EDC's presented here, unless noted otherwise, are normalized according to yield; that is, the area of the EDC's are proportional to the sample yield at the corresponding photon energies.

III. RESULTS

The standard procedure at the start of a study of surface states is to first prepare a clean surface either by cleaving in vacuum, by heat cleaning, or by ion bombardment and anneal. One then attempts to identify structure in the data which may not be explained by bulk electronic transitions By following the changes in this structure as the surface environment is altered by the adsorption of gases, one can try to associate the structure with the clean surface. In photoemission, it is possible to follow the movement of the surface position of the Fermi level as the crystal doping is varied from degenerate p-type to degenerate n-type. By studying the changes in pinning of the Fermi level, one can gain useful information as to the nature of the surface states in the forbidden energy gap, that is, where these states (filled or empty) are located and their density distribution. It is desirable to study as many crystals with different levels of doping as possible; however, since the III-V semiconductors are quite similar and there is good knowledge of the surface state distributions in some typical III-V semiconductors such as GaAs, one may feel fairly confident about obtaining a good picture of the surface state distributions in InP despite having studied a number of cleaves on one degenerate n-type crystal.

A.   Clean and Oxidized Surface

Figure 1 shows the EDC's at five different photon energies obtained from clean InP. All the structures in the EDC's appear to arise from bulk direct transitions since the initial and final state energies change with photon energy. By varying the incident photon
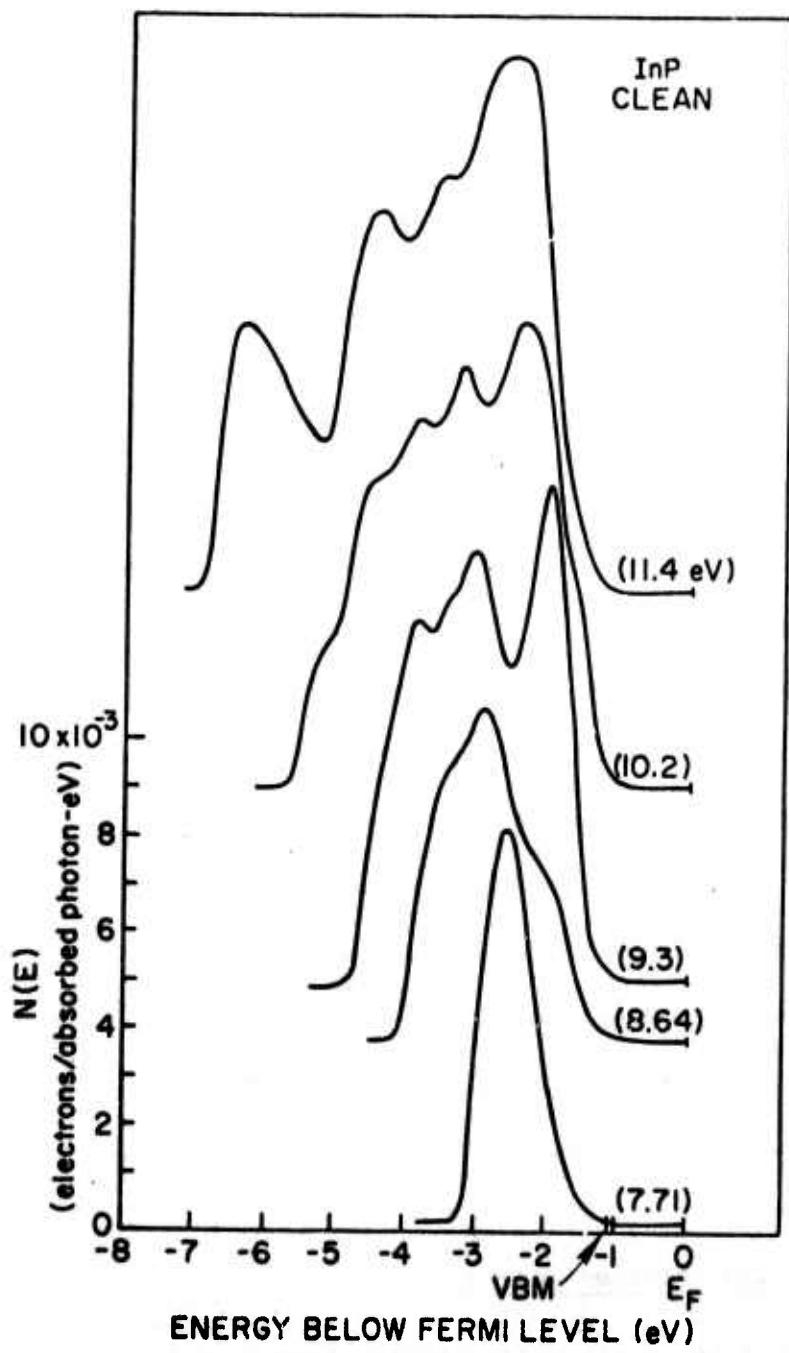
FIG. 1--EDCs for clean 6 X 10^{17} cm^{-3} n-type InP as a function of photon energy.

energy, these structures may be moved around to enhance small structures in the EDC's and thereby facilitate the identification of surface states, whose initial state energy does not vary with photon energy. In Si, a peak with constant initial state energy at different photon energies was observed; in InP, none could be found. The very faint shoulder near the high energy edge of the EDC at a photon energy of 10.2 eV is not visible at photon energies more than 0.5 eV above or below and is not due to emission from surface states. Rather, this is due to a direct transition from the top of the valence band near the Γ point in the Brillouin zone. The same transition is visible in GaAs.[4] The valence band maximum is therefore readily found by locating the high energy cutoff position of emission in the 10.2 eV EDC. A sampling of EDC's at various energies reveals that the high energy cutoff position lies closest to the Fermi level at photon energies near 10 eV, so this is further evidence that one has indeed located the valence band maximum relative to the Fermi level at the surface. The surface position of the Fermi level is found to be pinned at 1.1 eV above the valence band maximum--in rough agreement with Fischer[17]--putting the bottom of the pinning states at about 0.25 eV below the conduction band minimum (CBM), InP having a forbidden energy gap of 1.34 eV. The accuracy in these values, as mentioned previously, is to within ±0.1 eV. Note the absence of prominent structure near the valence band maximum which remains stationary relative to the Fermi level when the incident photon energy is varied, indicating an absence of sharp surface density of filled states at or near the forbidden gap which would give rise to a peak or shoulder with a constant initial state energy. The peaks here move with varying photon energy.

This situation is very similar to that in GaAs,[3] where the surface Fermi level is pinned at 0.7 eV below the conduction band minimum and, on the degenerate p-type sample, the surface Fermi level is at the bulk position indicating absence of filled surface states in the bandgap. Application of Harrison's Bond Orbital Model based on experiments by Gregory et al[3] shows the existence of two bands of surface-states with an energy difference of several electron volts between the two. The empty surface states are associated with the Ga and the filled surface states with the As atoms. A recent refinement[18] of the model of the GaAs surface includes a displacement of the outer layer of atoms. The As atoms move out, and the Ga atoms move in towards the lattice by almost a lattice constant. The dangling electrons on the As atom then become mostly S-like, and the empty states associated with the Ga atom become mostly p-like. Eastman and Freeouf[7] also produced evidence in a measurement on GaSb that the empty surface states are associated with the column III surface atoms and the filled surface states with the column V surface atoms. Calculations by Joanopoulos and Cohen[9] also show a splitting of the surface states associated with the fundamental gap of about 3 eV, with the lowest surface state band primarily localized on the surface As atoms and the highest surface state band localized primarily on the Ga surface atoms. Recent calculations by Calandra and Santoro[10] also show agreement. This picture naturally extends to InP as well, with the empty and filled surface states associated with the In and P, respectively. Previously, Gregory et al[3] have made similar associations in GaAs. On exposure to oxygen, the oxygen atoms are expected, to a first approximation, to bond to the P atoms and further lower the filled surface states and leave the empty surface

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states, and thus the Fermi level pinning, largely unaffected. The behavior of InP under oxidation is shown in Fig. 2. The EDC's are presented with the various peaks lined up. The crystal was very insensitive to oxygen, a normal behavior among the III-V semiconductors in this $h\nu$ range. The main effects up to 10^7 Langmuirs (IL = 10^{-6} torr-sec) of oxygen were a lowering of the leading peak and a rise in the background emission. Note, in particular, that there are no structures which disappear with light oxidation, as in the case of Si,[1] where the highest lying structure associated with the filled surface states disappeared upon exposure to about 10^3 L of oxygen. This lack of oxygen sensitive structures indicates that the filled surface states probably form a broad band lying several eV below the valence band maximum. The Fermi level position, to within experimental resolution (± 0.1 eV), remained constant up to 10^7 L. At 10^8 L, the EDC underwent a much larger change, and the structures began to become smeared out. At 10^9 L, a large oxygen peak has built up and most of the peaks were gone. Here, it has become rather difficult to line up the EDC's in the same manner as previously; nonetheless, it appears that the Fermi level pinning had not changed significantly even at this large exposure. This is consistent with the picture of oxygen initially bonding to the P atoms and leaving the empty surface states largely unaffected. In contrast, the Fermi level pinning in n-type Si is completely destroyed by exposure to 10^3 L O_2,[1,19] the pinning position rising from midgap to the bulk position. The Si "dangling bond" electrons bond with the oxygen atoms to remove the intrinsic surface states and form new interface states.
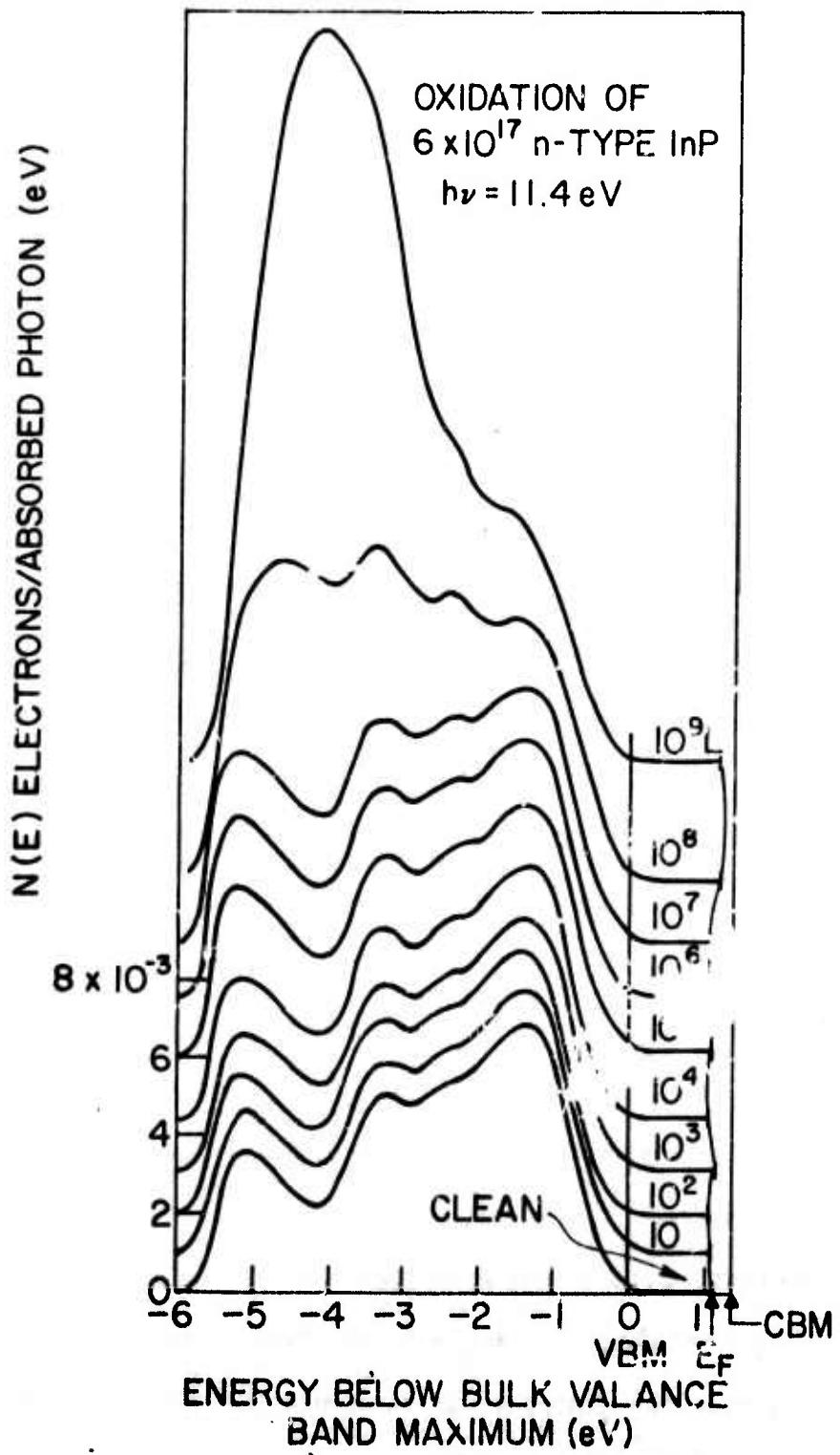
FIG. 2--EDCs for 6 X 10^{17} cm^{-3} n-type InP at a photon energy of

11.4 eV as a function of oxygen exposure.

B.   Cesiated Surface

Deposition of Cs permits one to study the metal-semiconductor interface and Schottky barrier pinning. Conventional Schottky barrier work does not shed much light on the origin of the pinning states, as studies are made with the metal already on the semiconductor surface. With UPS, we may study the Fermi level pinning as the metal is added in fractions of a monolayer. Since UPS probes about 20 Å into the bulk at around 10 eV, it is possible to use bulk semiconductor structures as a reference in following changes in the electronic structure at the surface. Cesium is particularly suitable for such studies as it is strongly polarized and the repulsion between the atoms prevents formation of islands on the surface, enabling it to wet the semiconductor well and provide a uniform coverage over the surface.[20]

One cleave of the sample was carefully cesiated in nine separate steps till maximum yield was achieved. Cesiation of a different cleave produced similar results. Sets of EDC's were taken after each exposure and the Fermi level position determined using the Cu backdoor as a reference. Figure 3 shows the movement of the surface Fermi level and the valence band maximum at the surface relative to the bulk peaks, as obtained from the 10.2 eV EDC's. The valence band maximum is determined from the extrapolated upper edge of the EDC taken at energies (around 10.2 eV) where direct excitations from the top of the valence band near Γ is visible as a faint shoulder in the EDC. The extrapolation is done by drawing a straight line along the leading edge of the EDC, cutting off the high energy tail. An example of this extrapolation is given in Fig. 4. The high energy tail may be caused by a number of reasons to be discussed later. In Fig. 4, a set of EDC's taken at 10.2
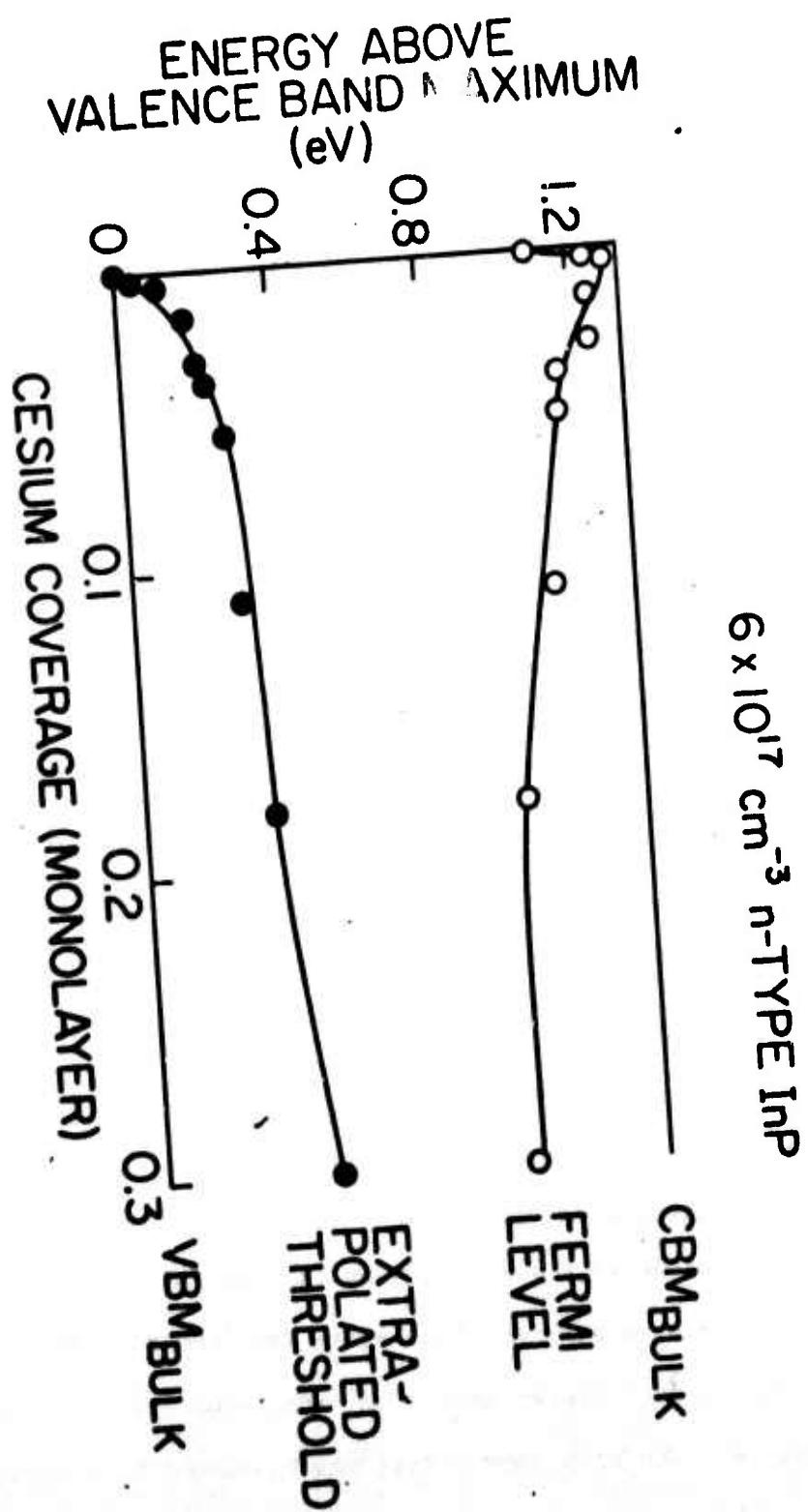
FIG. 3--Positions of the surface Fermi level and the extrapolated upper edge of the EDCs relative to the bulk band edges.

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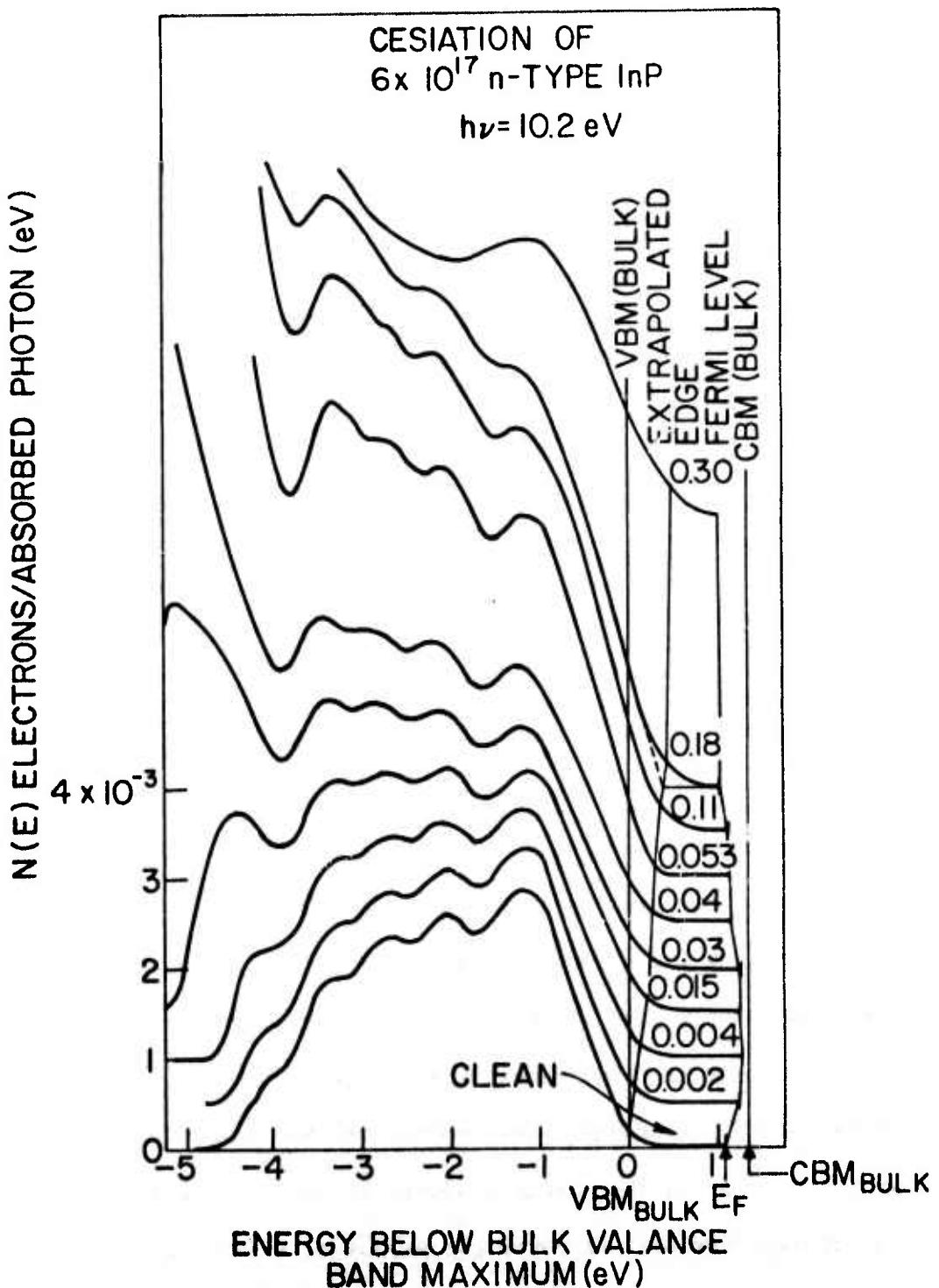
FIG. 4--EDCs at a photon energy of 10.2 eV as a function of cesium coverage.

eV for various stages of cesiation is shown. The bottom trace is taken from the clean surface; the cesiated EDC's are stacked above it and labeled with the coverages. The coverages are estimates based on GaAs as discussed in the experimental section. The EDC's are shown with the peaks due to bulk transitions lined up. The large background of scattered electrons may cause a shift in the position of the peaks, but the effect is small for the leading peaks because there are few scattered electrons at high energies. A subtraction of estimated background electrons confirms this. The Fermi levels at the surface and the extrapolated upper edge positions are also shown with lines drawn through the various points. Figure 5 shows the front (high energy) portions of EDC's for various cesium coverages and are scaled so that the leading peak heights are identical. The movement upwards in energy (into the bandgap) of the upper edge of the EDC with Cs is quite apparent. By the time maximum yield has been reached, the movement has reached 0.5 eV. The Fermi level, on the other hand, first showed an upward movement with very light (<1/100 monolayer) cesium coverage, then started dropping with further deposition of Cs, and by the last cesiation it has dropped to 0.1 eV below the pinning position on the clean surface. Heavy cesiation also caused the structures in the EDC's to disappear so that only the broadened first peak is still visible by the ninth cesiation. There was also considerable high energy tailing in the EDC's. Although the disappearance of structure at 0.3 monolayer made comparison with lower coverages difficu.., the movement upward of the upper edge of the EDC's was quite apparent even at coverages as low as 0.015 monolayer when all the peaks in the EDC were clearly visible. At a coverage of 0.11 monolayer when the upper edge had moved by almost 0.4 eV, all the bulk peaks

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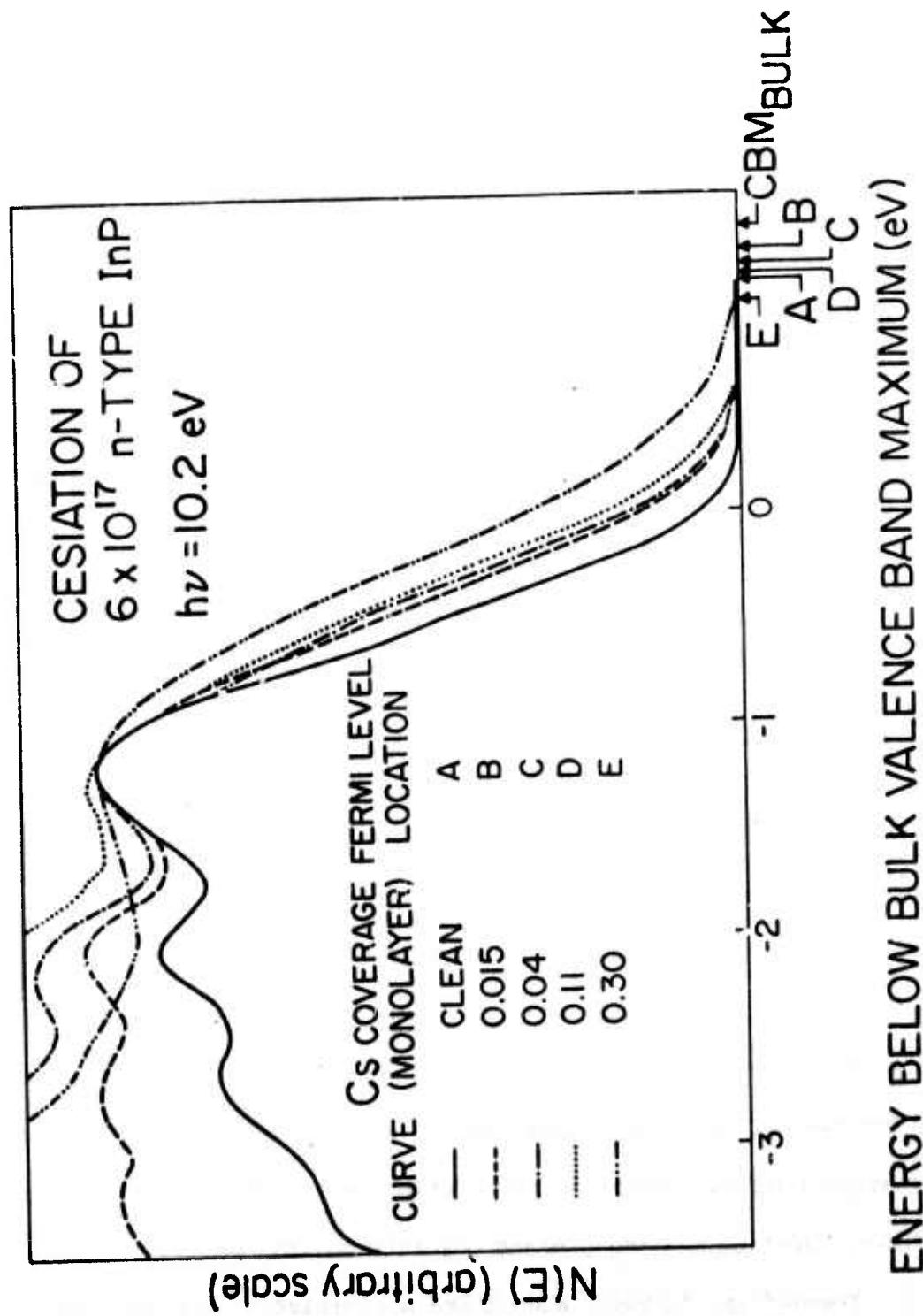
FIG. 5--The high energy portions of the EDCs at a photon energy of 10.2 eV as a function of cesium coverage.

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in the EDC were still visible, thus making comparison with EDC's at lower coverages easy. The same sort of behavior is observed at lower photon energies. Yield data for the various cesiated surfaces is shown in Fig. 6. The threshold on the clean surface is 5.78 eV, in close agreement with Fischer's[17] value of 5.69 eV and Williams and McGovern's[21] value of 5.6 eV. The minimum threshold obtained was 2.03 eV, which, when taking the upward movement of the valence band edge and the downward movement of the Fermi level into account, gives a value for the work function of 1.5 eV which is also close (within 0.1 eV) to Fischer's value. The various thresholds for the different cesiations were obtained from these curves, and the threshold lowering was used in estimating the cesium coverages.

InP is an interesting material in Schottky barrier studies in that it deviates quite far from the 2/3 rule of Mead et al,[5] who discovered that the Schottky barrier height with Au is approximately two-thirds of the bandgap down from the conduction band edge. The final pinning position found here falls at or slightly below the bottom of the empty surface states; in GaAs, the Fermi level with Cs coverage is also pinned about 0.1 eV below the bottom of the empty surface state band. It is likely that the final pinning position in the formation of Schottky barriers is closely related to where the pinning occurs on the clean surface since, for two different materials, one of which follows the 2/3 rule and one which does not, the same association between the clean surface Fermi level location and the pinning position may be made.

Freeouf and Eastman[7] also found a correlation between the empty surface state band and the Schottky barrier pinning position for a number of III-V materials. We agree with this to first order. However,

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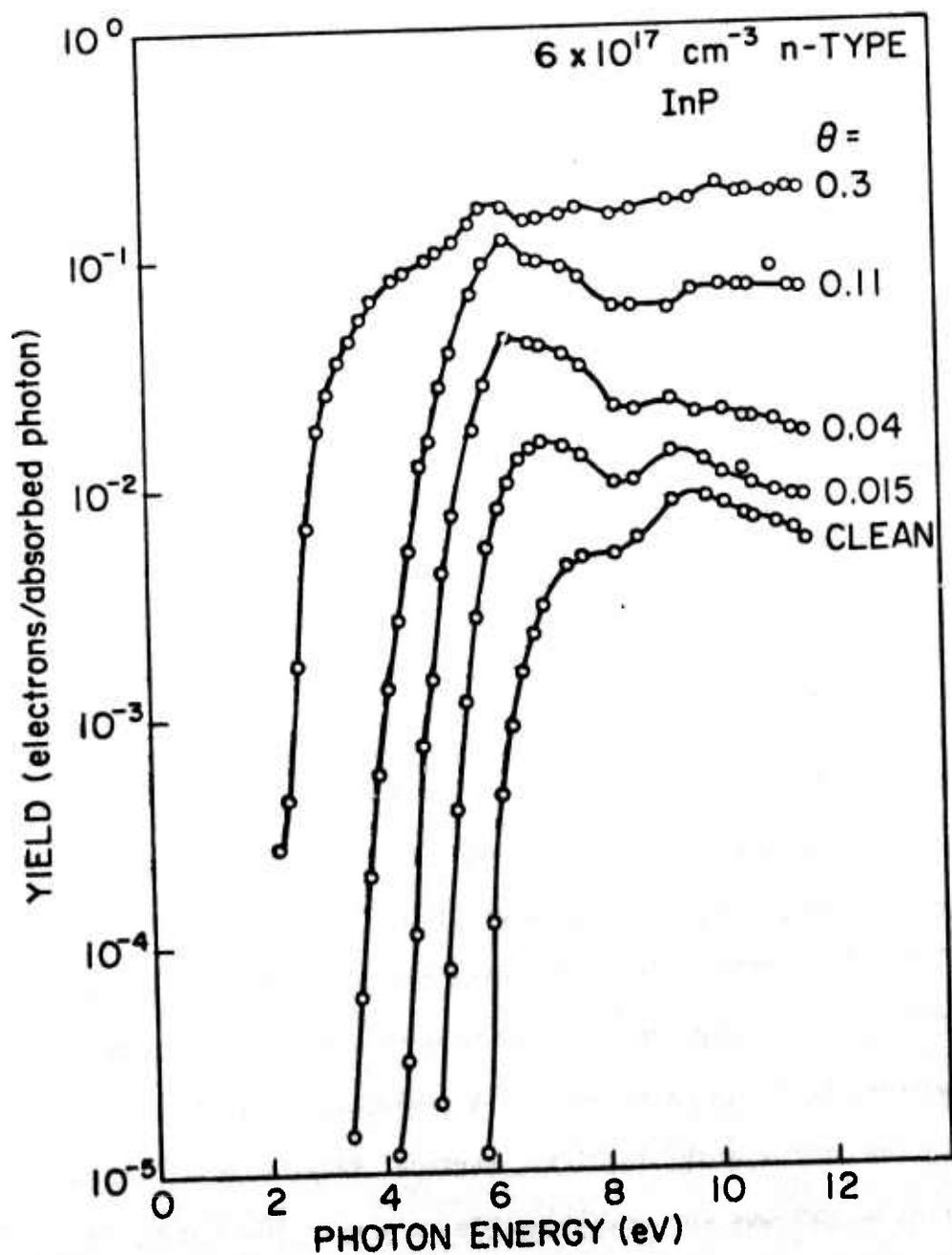
FIG. 6--Spectral yield curves for InP as a function of cesium coverage.

it appears that the Cs interacts with the semiconductor surface in such a way as to lower the pinning position to below the bottom of the empty surface state band and move the valence band threshold in the EDC (Fig. 3) to higher energy, and Schottky barrier pinning cannot be simply explained in terms of filling the empty surface states on the clean surface. Eastman and Freeouf based their conclusions on results on a number of III-V semiconductors including GaSb where they found the empty surface states to extend about 0.4 eV below the conduction band minimum so that the Schottky barrier pinning position corresponds closely to the bottom of the empty surface states. However, experiments by Chye et al[22] indicate an absence of empty and filled surface states in the bandgap in GaSb. Moreover, the Fermi level moved by almost the entire bandgap when Cs was added to the surface, indicating that a simple filling of empty surface states is an inadequate explanation. In arriving at their conclusions, Eastman and Freeouf also had to rely on the existence of a "tail" of empty surface states with a low density of states which might change when different metals were added to the sample surface. Gregory and Spicer[6] have found no evidence of such a "tail". Moreover, recently it has become clear that there is a variation in the location of the Fermi level on clean n-type GaAs samples studied in various laboratories.[3,7,23,24,25] Since the Fermi level can be pinned by as few as 10^{12} to 10^{13} surface states/cm^2, one must be careful in assuming that the pinning position on n-type III-V semiconductors is associated with the bottom of the empty intrinsic surface states. While the pinning position on InP was very reproducible, and near the top of the band gap, suggesting that the pinning states were intrinsic (one might expect pinnin, due to surface roughness and defects to vary from cleave

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to cleave, and might also expect impurities to pin the Fermi level somewhat further down in energy), at present it is impossible to rule out pinning by extrinsic states associated with various factors such as surface roughness or impurities. The large movement of the valence band maximum on InP is indicative of a strong interaction between the Cs and the semiconductor surface. Small amounts of Cs go on the surface as positive ions and creates a negative space charge layer, causing the initially bent bands to straighten giving rise to an upward movement of the Fermi level. As more and more Cs is added, the strong interaction causing the extension of emission into the bandgap cannot be simply explained. One possible mechanism is the type suggested by Inkson[23] -- i.e., when a metal is put on a semiconductor, it gives rise to an image potential which attracts electrons in the conduction band causing the conduction band to bend downward and attracts holes in the valence band causing the valence band to move upward, resulting in a narrowing of the bandgap. The data presented here does not support this picture unequivocally, but a similar sort of mechanism may be at work. More theoretical work dealing with the interaction of Cs with semiconductors is clearly needed before the data can be completely explained. One might ask if the interaction and broadening of the leading peak in the EDC's might be due to experimental artifacts. The resolution of the energy analyzer can be tested by observing the Fermi edge broadening of the EDC's taken off the copper backshutter. In all cases, the width of the 10%-90% edge height was between 0.2 eV and 0.3 eV (increasing with increased Cs coverage), too small to account for the observed broadening of the first peak in the EDC's. A second possibility is contamination due to outgassing during

cesiation. This is unlikely, for in GaAs where the same broadening with cesiation was observed, contamination caused a decrease in the broadening in the first peak rather than an increase. It might also be argued that the broadening is a peculiarity of a particular cleave, as some cleaves exhibited sharper structure than others; for example, the Γ transition used to determine the top of the valence band is visible as a faint shoulder on some cleaves but not on others. However, since Cs was applied to two different cleaves, one with a clearly visible shoulder from the Γ transition, and the other without such a shoulder, and since the same behavior under cesiation was observed on both, this possibility may be ruled out. Uneven coverage of Cs over the surface would cause a nonuniformity in work function over the surface, but this would only broaden the low energy edge of the EDC's. Uneven coverage would also lead to differences in bandbending over the surface. This difference is, however, small, as can be seen from Fig. 3, which shows Fermi level pinning changes and hence bandbending changes as a function of coverage. In any case, with heavy Cs deposition, the nonuniformity should disappear and with that, the broadening. Emission from the entire bandbending region may, at first glance, explain the broadening; however, on GaAs, differently doped crystals show the same broadening,[4] and on one sample doped 1.5 X 10^{17} p-type, the bandbending length, estimated using the depletion approximation, is much greater than the electron escape depth. The same is true for the InP sample here. Therefore, there must be some other mechanism, other than the unscreened acceptors, causing a bandbending sharp enough to yield the observed broadening, which again points to mechanisms such as Inkson's. If there were a sharp bandbending upward

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near the surface caused by the metal image potential, then the resulting EDC's would be broadened and structureless, and there would be emission from within the bandgap, as was observed. This sharp upbending of the bands would bring the valence band edge over a very short distance (several atomic layers) to the Fermi level at the surface and could explain the high energy tail up to the Fermi level observed in the EDC's taken from the heavily cesiated sample. This high energy tail is unlikely to be produced by emission from metallic Cs[24] because a superposition of an InP EDC and a Cs EDC does not lead to anything like the heavily cesiated InP EDC. Moreover, the yield from the high energy tail is much higher than the yield from metallic Cs. Metallic Cs has a very short electron escape depth and low yield at 10.2 eV.[25,26] For example, n(E) at the peak near the Fermi level in the Cs EDC's is more than two orders of magnitude smaller than n(E) at the first bulk peak in the InP EDC's. It is therefore unlikely that emission from bulk Cs changes the high energy edge of the EDC significantly.

IV. CONCLUSIONS

A careful study of a n-type InP crystal has demonstrated the absence of emission from filled surface states with strongly peaked density of states. A broad band of filled surface states may lie below the valence band maximum, however. Fermi level pinning due to a band of empty surface states extending 0.25 eV into the bandgap was observed. The compound was insensitive to oxygen exposure, and the Fermi level pinning position changed little with oxidation up to exposures as large as 10^7 L O_2. This is consistent with the model proposed by Gregory et al,[3]

where the empty surface states may be associated with the column III element, and the filled surface states associated with the column V element, with the two bands of surface states separated by a rather large bandgap. The oxygen bonds onto the column V atoms and leaves the empty surface states undisturbed for the first exposures of oxygen. The downward bandbending in InP that was observed with the arrival of the first small fraction of a monolayer of Cs was due to the presence of Cs^+ ions on the surface. With more Cs, there was a definite upward movement of the upper edge of the EDC's, and the Fermi level moved downward and stabilized at or just below the pinning position on the clean surface. This indicates that the Cs interacts with the semiconductor in some complicated manner beyond a simple donation of electrons to the empty surface states. The Schottky barrier model of Inkson[23] which predicts a closing of the bandgap near the surface due to image potentials would partly explain the phenomenon. It is clear, however, that much more theoretical and experimental work has to be done before this phenomenon may be understood completely.

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CHAPTER 5

The following is a brief summary of the GaSb paper in preparation. Part of this paper was included in the last semi-annual report and has been published.[1] The results to be discussed include work on clean O_2 and CO adsorbed, and Cs, Cs_xO_y and K covered surfaces of GaSb.

EDCs taken on clean, cleaved n- and p-type GaSb (110) surfaces showed no structure associated with filled surface states, similar to GaAs and InP. However, Fermi level (E_F) pinning was not observed on the cleaved surface, while others[2,3] observed pinning on n-type samples. This disagreement can be explained by using the n-GaSb oxidation data, which shows that E_F moves downward through the bandgap by about 0.55 eV with light oxidation at coverages estimated to be << 1 monolayer. A similar behavior of E_F was observed with deposition of Cs and K. These results suggest a relaxation of the n-type GaSb (110) surface upon adsorption of a small amount of foreign matter; that is, the foreign atoms "catalyze" a relaxation of the surface atoms causing the empty surface state levels to shift in energy and pin E_F at approximately the same position regardless of the kind of foreign atom. With increasing coverage of the foreign atoms, the pinning states shift in energy and the final pinning positions are different. Oxidizing the n- and p-type samples caused no selective disappearance of structure that may be attributed to filled surface states. The critical stage of oxidation appears to be at 10^5L, where the E_F position reaches a minimum in the bandgap and where relatively large changes in the EDCs and electron affinity are first seen. Most striking is the recent data taken at the Stanford Synchrotron Radiation Project at $h\nu$ = 21 and 25 eV, where a

huge oxygen peak first appears at 10^5L O_2 exposure. The same movement of E_F downward was observed with synchrotron radiation. Beyond 10^5L, E_F moves upward slightly on both n- and p-type samples.

CO adsorption on p-type GaSb was studied. Here the behavior is similar to GaAs to the extent that very large exposures ($> 10^7$L) is necessary to produce a change in the EDCs, but the gas does not desorb while it desorbs completely from the surface of GaAs in a matter of hours.

Cs and K on n-type GaSb shifts the Fermi level down from the conduction band minimum (CBM) to near the valence band maximum, with approximately the same amount of movement of E_F as in oxygen covered n-type GaSb. The interaction between Cs and GaSb appears to be weaker than that between Cs and InP or GaAs. For example, the movement upwards of the upper edge of the EDCs in Cs covered GaSb is seen at heavier coverages than those which induced large movements on InP and GaAs. Moreover, GaSb cesiated to attain maximum "white light" yield cannot retain all the Cs, i.e., some of the Cs desorbs. The EDC at near optimum coverage also looks different and has a narrow leading peak which is different in nature from the leading peaks at lower Cs coverages. Oxidizing the Cs covered samples immediately led to EDCs with structure like Cs-oxides, whereas for GaAs numerous cycles of Cs-O_2 treatments are necessary to produce Cs-oxide like structure in the EDCs.

Our work on GaSb as summarized above demonstrates directly for the first time that Schottky barrier pinning on a III-V material is not produced by intrinsic surface states characteristic of the clean surface but is produced by metal induced (extrinsic) states. This work also supports the GSCH model developed earlier that associates the empty surface states with the column III surface atoms and the filled surface states with the column V surface atoms with a large bandgap between the two kinds of surface

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states . Important differences in surface chemistry has been found between GaSb and the other two III-V semiconductors, GaAs and InP, studied by us. This shows that materials that may appear to be very similar may not bear the slightest resemblance to each other in some properties. Therefore, certain practical devices may be possible with certain materials but not with others, and to find the right materials it is extremely important to know how each material behaves under different surface conditions.

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CHAPTER 6

FERMI ENERGY PINNING AT SURFACES WITHOUT MIDGAP STATES

Recent photoemission studies[1,2] have related Fermi-energy pinning to observed surface states. Such a relation was proposed initially by Bardeen[3] and has seemed plausible since dangling hybrid states might be expected to occur there. Indeed photoemission studies appear to have detected such states.[4] However, a recent theoretical study of surface reconstruction[5] concluded that the two-by-one reconstruction on a silicon (111) surface consists of _large_ displacements which drop alternate dangling hybrids deep into the valence band and raise the others near to or into the conduction band; the former would be doubly occupied, the latter empty. This would at first suggest that the Fermi energy should not be pinned on ideal semiconductor surfaces and the observation of pinning could then be used as evidence for nonideal attributes of the surface (such as steps or contamination). We will in fact see that pinning is to be expected whether or not there are surface states present.

The driving force for the reconstruction was the dehybridization energy which would be a very small effect if the dangling hybrids were singly occupied, but becomes very large after the electron transfer. In a pure (intrinsic) semiconductor, half of the dangling hybrids go each way leaving a neutral surface and no band bending. In an n-type semiconductor, on the other hand, a considerable dehybridization energy would be gained by placing two electrons from the conduction band in one of the empty dangling hybrid states and reversing its reconstruction to drop that level deep into the valence band. In fact, the energy gained is greater than that for the intrinsic case by an energy per pair equal to the band gap. This gain would be reduced by electrostatic contributions

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due to breaking the alternate pattern of reconstruction, but presumably the two-by-one reconstruction is broken into domains in any case and adding the extra charges at the domain boundaries would not cause a serious change in electrostatic energy. The net effect is to leave the surface negatively charged, raising the bands at the surface. Similarly in a p-type semiconductor we would expect a doubly occupied hybrid to give its electrons to the valence band, reverse reconstruction, and move up near the conduction band. In either case the process should continue until there are negligible numbers of electrons or holes, fixing the Fermi energy midgap.

This effect need not be disrupted by surface contamination. For example, atomic oxygen is expected to chemisorb to the surface without modifying the neutrality of the surface for pure semiconductors.[4] Similarly, it would not modify the charging of the surface on a doped semiconductor, leaving the pinning as is. There is at work the same general effect which tends to sweep states from the gap in amorphous semiconductors; the system rearranges or deforms to drop the energy of occupied states and raise that of empty states. However, one could imagine that adsorbed hydrogen, for example, might saturate the dangling hybrids sufficiently stably to prevent any Fermi energy pinning; that seems uncertain.

The situation on polar semiconductors is quite different. On the (110) surface of gallium arsenide the arsenic atoms are expected to move outward with doubly occupied hybrids and the gallium atoms to move inward with empty dangling hybrids.[4.6] The counterpart of the modification of reconstruction given above for n-type silicon would be the outward movement of a gallium atom and the double occupation of its dangling hybrid.

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The considerably lower electronegativity of the gallium would work against this and would seem to explain the observed lack of pinning on clean gallium phosphide[7] and gallium arsenide[8] surfaces.

This discussion does not argue directly against the existence of surface states in the gap, but only indicates that they are not necessary to an understanding of pinning. Out theoretical study of reconstruction[5] indicates that no such surface states are expected on ideal reconstructed surfaces, but the photoemission studies have been interpreted as indicating that they are there on experimental surfaces.[4]

The author is indepted to J. Van Laar and W. E. Spicer for discussions of this problem.

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8. W. E. Spicer, I. Lindau, P. E. Gregory, C. M. Garner, P. Pianetta and P. W. Chye, to be published.

CHAPTER 7

FUTURE WORK

In the immediate future the enormous amount of data obtained at SSRP will be carefully analyzed and the results will be submitted for publication. Correlations will be attmepted between such parameters as the element used for bulk dopant and etch pit density on the cleaved surface and whether or not pinning on GaAs was observed. A new chamber under construction for studying other faces is near completion. Sample preparation is by heating and/or sputtering, and Auger electron spectroscopy is used to monitor sample cleanliness. The GaAs (111) B face will be studied first. At SSRP work will continue on the cleavage faces with more emphasis on Schottky barrier studies of the III-V's, using, in particular, photoemission partial yield spectroscopy. This will be supplemented by photoemission spectroscopy. Attempts on other faces, as well as on ternary or quaternary alloys, will also be made.

APPENDIX

A. Articles published in the last six months:

W. E. Spicer and P. E. Gregory, CRC Critical Reviews in Solid State Sciences 5, 231 (1975), "Surface and interface electronic structure of GaAs and other III-V compounds." (Invited paper presented at the Second Annual Conference on the Physics of Compound Semiconductor Interfaces).

P. E. Gregory and W. E. Spicer, Phys. Rev. B12, 2370 (1975), "Photoemission studies of the GaAs-Cs interface."

W. E. Spicer, P. E. Gregory, P. W. Chye, I. A. Babalola and T. Sukegawa, Appl. Phys. Lett. 27, 617 (1975), "Photoemission study of the formation of Schottky barriers".

P. E. Gregory and W. E. Spicer, Phys. Rev. B13, 725 (1976), "Photoemission study of surface states of the (110) GaAs surface".

P. E. Gregory and W. E. Spicer, J. Appl. Phys. 47, 510 (1976), "Ultra-violet photoemission study of cesium oxide fibers on GaAs."

P. E. Gregory and W. E. Spicer, Surf. Sci. 54, 229 (1976), "Photoemission study of the adsorption of O_2, CO and H_2 on GaAs (110)".

W. E. Spicer, P. W. Chye, P. E. Gregory, T. Sukegawa and I. A. Babalola, J. Vac. Sci. Technol. 13, 233 (1976), "Photoemission studies of surface and interface states on III-V compounds." (Invited paper presented at the 21st National Vacuum Symposium).

P. W. Chye, I. A. Babalola, T. Sukegawa and W. E. Spicer, Phys. Rev. Lett. 35, 1602 (1975), "GaSb Surface States and Schottky-Barrier Pinning."

B. Articles accepted:

P. W. Chye, I. A. Babalola, T. Sukegawa and W. E. Spicer, Phys. Rev. b, "Photoemission Studies of surface states and Schottky barrier formation on InP".

W. E. Spicer, I. Lindau, P. E. Gregory, C. M. Garner, P. Pianetta and P. W. Chye, J. Vac. Sci. and Technol. "Synchrotron radiation studies of electronic structure and surface chemistry of GaAs, GaSb and InP". (Invited paper presented at the Third Annual Conference on the Physics of Compound Semiconductor Interfaces).

C. Article submitted:

W. A. Harrison, "Fermi energy pinning and surfaces without midgap states".